September, 2000

RT3D Tutorials for GMS 3.1 Users (Draft Version)

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CHAPTER 1

Introduction

RT3D (Reactive Transport in 3-Dimensions) is a computer code that solves coupled partial differential equations that describe reactive-flow and transport of multiple mobile and/or immobile species in a three dimensional saturated porous media. This GMS 3.1 compatible version of RT3D (version-2 beta) was developed from the public domain transport code MT3DMS. As with MT3DMS, RT3D also uses the USGS groundwater flow model MODFLOW for computing spatial and temporal variations in groundwater head distribution.

This report presents a set of tutorial problems that are designed to illustrate how RT3D simulations can be performed within the Department of Defense Groundwater Modeling System (GMS). GMS serves as a pre- and post-processing interface for RT3D. GMS can be used to define all the input files needed by RT3D code, and later the code can be launched from within GMS and run as a separate application. Once the RT3D simulation is completed, the solution can be imported to GMS for graphical post-processing.

RT3D supports several reaction packages that can be used for simulating different types of reactive contaminants. Each of the tutorials, described below, provides training on a different RT3D reaction package. Each reaction package has different input requirements, and the tutorials are designed to describe these differences. Furthermore, the tutorials illustrate the various options available in GMS for graphical post-processing of RT3D results. Users are strongly encouraged to complete the tutorials before attempting to use RT3D and GMS on a routine basis.

1.1   Other Documents

There are several other documents describing GMS and RT3D. The GMS *Reference Manual* is a complete reference on GMS and includes a chapter describing the RT3D interface. The RT3D *Reference Manual* provides a detailed discussion of the equations, numerical methods, file formats, and other issues related to the RT3D model.

In addition to the GMS and RT3D manuals, the GMS *Tutorials* document contains a set of tutorials similar to the tutorials described in this document. These tutorials describe basic operation of GMS and include tutorials on MODFLOW, MT3DMS, MODPATH, FEMWATER, and other models supported in GMS. While it is not essential, it is recommended that the new user complete the MODFLOW and MT3DMS tutorials before beginning the RT3D tutorials contained in this document. The GMS *Tutorials* document does not contain RT3D tutorials. All RT3D tutorials are contained in this document.

1.2   Organization

The first tutorial (*Chapter 2 - Instantaneous Aerobic Degradation*) includes a description of how to build both the flow and the transport model within GMS. The remaining tutorials use a pre-defined flow model and only describe the construction of the transport model. Although the tutorials may be completed in any order, it is generally best to complete the first tutorial before attempting to complete any of the remaining tutorials.

1.3   Demo vs. Normal Mode

GMS utilizes a copy protection system wherein different components of the GMS interface may be licensed and activated separately. Modules and interfaces that have been licensed are enabled using the *Register* command in the *File* menu. The icons for the unlicensed modules or the menus for model interfaces are dimmed and cannot be accessed.

GMS provides two modes of operation: demo and normal. In normal mode, the modules and interfaces you have licensed are undimmed and fully functional and the items you have not licensed are dimmed and inaccessible. In demo mode, all modules and interfaces are undimmed and functional regardless of which items have been licensed. However, all of the print and save commands are disabled. While some of the tutorials in the GMS *Tutorials* document can be completed in demo mode, all of the tutorials in this document must be completed in normal mode.

CHAPTER 2

Instantaneous Aerobic Degradation

This tutorial illustrates the steps involved in performing a reactive transport simulation using the RT3D model. Several types of contaminant reactions can be simulated with RT3D by using a pre-defined or user-defined reaction package. The reaction simulated in this tutorial is instantaneous aerobic degradation of hydrocarbons using a pre-defined user reaction package

2.1 Description of Problem

The problem we will be solving in this tutorial is shown in Figure 2.1. The site is a 510 m X 310 m section of a confined aquifer with a flow gradient from left to right. An underground storage tank is leaking fuel hydrocarbon contaminants at 2 m^3/day at the location shown. Concentration of the hydrocarbons is 1000 mg/L and the spill may be assumed to be devoid of oxygen. Details of the aquifer hydrology and geometry are given below. Initial levels of hydrocarbon and oxygen in the aquifer are 0.0 and 9.0 mg/L, respectively. We will simulate a continuous spill event and compute the resulting hydrocarbon and oxygen contours after one year using instantaneous degradation kinetics.

The first part of the problem will be to compute a flow model of the site using MODFLOW. Using the flow field computed by MODFLOW, a reactive transport model will then be defined using RT3D.
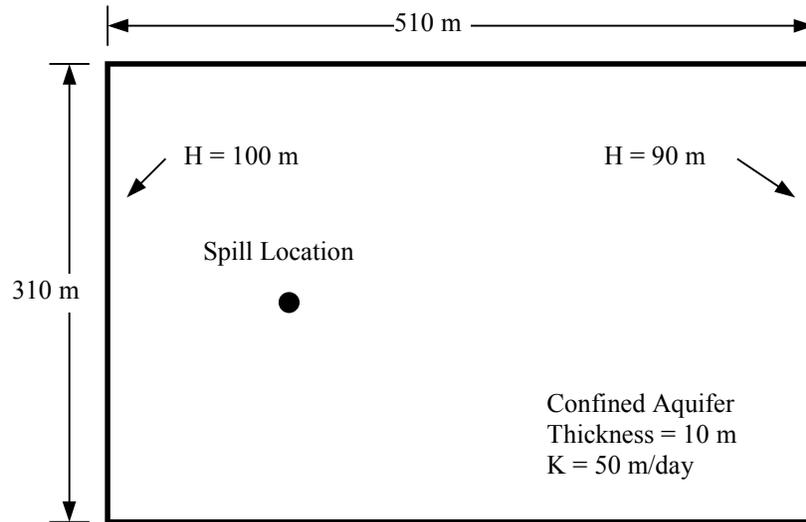
Figure 2.1   Sample Problem to be Modeled with RT3D.

2.2   Description of Reaction

The reaction model we will be using simulates the instantaneous degradation of fuel hydrocarbons under aerobic conditions based on the following reaction (benzene basis):

$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2.1)$$

Therefore, the mass ratio of benzene to oxygen, F, is 3.08 (i.e. 3.08 g of oxygen to 1 g of benzene). The instantaneous removal of either contaminant (H) or oxygen (O) is dictated by the following algorithm, where t refers to a particular time step:

$$H(t+1) = H(t) - O(t)/F \text{ and } O(t+1) = 0, \text{ when } H(t) > O(t)/F \dots\dots(2.2)$$

$$O(t+1) = O(t) - H(t) \bullet F \text{ and } H(t+1) = 0, \text{ when } O(t) > H(t) \bullet F \dots\dots(2.3)$$

Given this algorithm, either hydrocarbon or oxygen concentration in a given grid cell will be reduced to zero at each time step, depending on which component is stoichiometrically limiting in the prior time step.

2.3   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.

2.4   Required Modules/Interfaces

This tutorial utilizes the following components of the GMS interface:

- The *3D Grid* module

- The MODFLOW interface

- The RT3D interface

You can confirm whether each of these components has been enabled on your copy of GMS by selecting the *Register* command from the *File* menu. If you have licensed and enabled each of the listed items on your version of GMS, you can proceed to complete the tutorial in normal mode. If not, you will need to obtain an updated password or hardware lock before continuing.

2.5   Building the MODFLOW Model

The first part of the simulation is to build a MODFLOW flow model. In this case, a steady state flow model will be used with the transport simulation.

2.5.1   Conceptual Model Approach vs. Grid Approach

In many cases, the most efficient way to create a MODFLOW simulation is to build a conceptual model of the site using the feature objects in the *Map* module. However, since this problem is a simple rectangular model, we will use the grid approach and edit values directly on the cells.

2.5.2   Creating the Grid

The first step in defining the MODFLOW simulation is to create a single layer grid.

1. Switch to the *3D Grid Module*

2. Select the *Create Grid* command in the *Grid* menu.

3. In the *X dimension* section, enter 510 for the length and 51 for the number of cells.

4. In the *Y dimension* section, enter 310 for the length and 31 for the number of cells.

5. In the *Z dimension* section, enter 1 for the number of cells (the length in Z does not matter).

6. Select the *OK* button.

At this point, you should see a grid appear.

2.5.3   Initializing the Model

First, we will initialize the MODFLOW data.

Select the *New Simulation* command from the *MODFLOW* menu.

2.5.4   The Basic Package

The next step is to define the data in the MODFLOW Basic Package.

Units

First, we will define the units.

1. Select the *Basic Package* command from the *MODFLOW* menu.

2. Select the *Units* button.

3. For the *Length* unit, select *m*.

4. For the *Time* unit, select *d*.

5. For the *Mass* unit, select *mg*.

6. For the *Force* unit, select *N*.

7. For the *Concentration* unit, select *mg/l*.

8. Select the *OK* button.

Note that these same units are used for the transport simulation.

Starting Head

Next, we will define an initial condition of 100 m everywhere in the grid.

1. Select the *Starting Heads* button.

2. Select the *Constant -> Grid* button.

3. Enter a value of 100.

4. Select the *OK* button.

5. Select the *OK* button to exit the *Starting Heads* dialog.

We need to change some values in the IBOUND array to designate the constant head boundaries. However, we will do this later by selecting the cells and using the *Cell Attributes* command. Thus, we are finished with this dialog.

Select the *Close* button to exit the *Basic Package* dialog.

2.5.5   The BCF Package

Next, we will define the data in the BCF package. Our model has a single unconfined layer. We will use the *True Layer* option to enter the layer parameters.

1. Select the *BCF Package* command from the *MODFLOW* menu.

2. In the *Layer type* section, select the *Confined* option.

For the layer elevations, we will enter a value of 10.0 m for the top elevation. The bottom elevation is at zero, which is the default, so we don't need to enter this value. We will also enter a K value of 50 m/day.

1. Select the *Top Elevation* button.

2. Select the *Constant -> Layer* button.

3. Enter a value of 10.

4. Select the *OK* button.

5. Select the *OK* button to exit the *Top Elevation* dialog.

6. Select the *Horizontal Hyd. Conductivity* button.

7. Select the *Constant -> Grid* button.

8. Enter a value of 50.

9. Select the *OK* button.

10. Select the *OK* button to exit the *Horizontal Hyd. Conductivity* dialog.

The rest of the default options in the package should be sufficient.

Select the *Close* button to exit the *BCF Package* dialog.

2.5.6   Defining the Spill Well

The spill will be simulated by defining an injection well at the location of the spill with a small injection rate.   During the transport simulation, a concentration will be assigned to the well. To define the well:

1. Select the *Select Cell* tool

2. While watching the I, J fields in the *Edit Window*, locate and select the cell at I=16, J=16, K=1.

3. Select the *Point Sources/Sinks* command from the *MODFLOW* menu.

4. Select the *Add* button in the *Well* section.

5. Enter a value of 2.0 for the *Flow*.

6. Select the *OK* button to exit the *Point Source/Sink* dialog.

2.5.7   Assigning the Head BC

The final step before running MODFLOW is to assign the constant head boundary conditions (BC) on the left and right sides of the model. First, we will assign the head BC on the left side.

1. Select the *Select J* tool

2. Select the leftmost column in the grid by clicking in any of the cells in the column.

3. Select the *Cell Attributes* command in the *MODFLOW* menu.

4. Enter -1 for the *IBOUND* value and leave the *Starting Head* at 100.0.

5. Select the *OK* button.

Next, we will assign the head BC on the right side.

1. Select the rightmost column in the grid by clicking in any of the cells in the column.

2. Select the *Cell Attributes* command in the *MODFLOW* menu.

3. Enter -1 for the *IBOUND* value and enter 99 for the *Starting Head* value.

4. Select the *OK* button.

2.5.8   Running MODFLOW

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

1. Select the *Save As* command from the *MODFLOW* menu.

2. In the *Save As* dialog, locate and open the directory entitled *tutorial\rt3d\btexins1*.

3. Enter "flowmod" for the name of the simulation.

4. Select the *Save* button.

To run MODFLOW:

1. Select the *Run MODFLOW* command from the *MODFLOW* menu.

2. Select *OK* at the prompt.

3. When the simulation is finished, close the window and return to GMS.

2.5.9   Viewing the Results

Next, we will read in the computed head file and view the head contours to ensure the validity of the solution.

1. Select the *Read Solution* command from the *MODFLOW* menu.

2. Select *OK* at the prompt.

You should see a series of contours indicating a flow from left to right.

2.6   Building the Transport Model

Now that the flow model is established, the next step is to perform the RT3D simulation. For this part of the simulation, we will select the reaction, define the reaction data, define the supplemental layer data needed by RT3D, and assign concentrations to the well.

2.6.1   Initializing the Model

The first step is to initialize the RT3D data.

Select the *New Simulation* command in the *MT3D* menu.

2.6.2   The BTN Package

Next, we will enter the data for the Basic Transport Package. First, we will select RT3D as the transport model and select the appropriate packages.

1. Select the *Basic Transport Package* command from the *MT3D* menu.

2. Select the *RT3D* option.

3. Select the *Packages* button.

4. Select the *Advection Package*, the *Dispersion Package*, the *Source/Sink Mixing Package*, and the *Chemical Reaction Package*.

5. For the reaction type, select the *Inst. Aerobic Deg. of BTEX* option.

6. Select the *OK* button to exit the *Packages* dialog.

Starting Concentrations

Note that in the *Layer data* section of the dialog, the species associated with the reaction we are modeling are listed by name. The next step is to define the starting concentration for each of these species. By default all of the starting concentrations are zero. This is the correct concentration for BTEX. For oxygen, we will define an ambient concentration of 9.0 mg/L.

1. Select the *Oxygen* species in the list above the *Starting Concentration* button.

2. Select the *Starting Concentration* button.

3. Select the *Constant -> Grid* button.

4. Enter a value of 9.0 and select *OK*.

5. Select the *OK* button to exit the *Starting Concentration* dialog.

Porosity

Next, we will define the porosity. The aquifer is a uniform horizontal aquifer with a top elevation of 10 m, a thickness of 10 m, and a porosity of 0.3. Since 0.3 is the default porosity assigned by GMS, no changes need to be made.

Stress Periods

Next, we will define the stress periods. Since the injection rate and the boundary conditions do not change, we will use a single stress period with a length of 730 days (two years).

Select the *Stress Periods* button.

Since there is already one stress period by default, we will simply change the length of the stress period

1. Enter a value of 730 for the *Length*.

2. Enter a value of 10 for the *No. of time steps*.

3. Select the *OK* button to exit the *Stress Periods* dialog.

Output Options

Finally, we will define the output options. One binary solution file is created by RT3D for each of the species. By default, RT3D saves a solution at each transport step for each species. Since this results in large files containing more solutions than we need for the simple post-processing we intend to do, we will specify that a solution be saved every 73 days (every time step).

1. Select the *Output Control* button.

2. Select the *Print at specified times* option.

3. Select the *Times* button.

4. Select the *Initialize Values* button.

5. Enter 73.0 for the *Initial time step size*.

6. Enter 73.0 for the *Maximum time step size*.

7. Enter 730.0 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.

This completes the input for the Basic Transport package.

Select the *Close* button to exit the *Basic Transport Package* dialog.

2.6.3   Assigning Concentrations to the Left Boundary

The left boundary of the model is a constant head boundary. Since the head at the left boundary is greater than the head at the right boundary, the left boundary acts as a source and water enters the model from the left. Thus, we must define the concentrations of our species at the left boundary. Otherwise, the water entering the model will have the default concentration (zero) for each of the species. This is often true for most species, but there are exceptions. For our model, the incoming fluid should have an ambient oxygen concentration of 9.0 mg/L. The oxygen concentration can be assigned one of two ways:

1. The cells at the boundary can be marked as specified concentration cells by changing the ICBUND value at the cells to –1.

2. The concentration of the incoming fluid at the boundary can be defined using the Source/Sink Mixing package.

The first method requires the fewest number of steps to set up. As long as the boundary acts as a source throughout the simulation, either of these approaches will achieve the same result. However, if the boundary acts as a sink during any part of the simulation, the second option should be used. With the second option, if the boundary switches to a sink due to changing heads in the interior of the model, the concentrations at the cells would be computed by RT3D. With the first option, the concentrations at the cells are fixed, regardless of the flow direction.

For our problem, the flow field is steady state and we know that the boundary acts as a source. Thus, we will use the first option. To mark the cells as specified concentration cells:

1. Select the *Select Cells* tool

2. Select the cells on the left boundary by dragging a box that just surrounds the cells.

3. Select the *Cell Attributes* command in the *MT3D* menu.

4. Change the *ICBUND* value to –1.

5. Select the *OK* button.

Note that we do not need to change the starting concentration values, since the values are already assigned via the starting concentration arrays.

2.6.4   The Advection Package

The next step is to initialize the data for the Advection package. We will be using the MOC method. Since this is the default method, no changes need to be made.

2.6.5   The Dispersion Package

Next, we will enter the data for the Dispersion package. The aquifer has a longitudinal dispersivity of 10.0 m and a transverse dispersivity of 3.0 m. The vertical dispersivity is assumed equal to the longitudinal dispersivity.

1.   Select the *Dispersion Package* command in the *MT3D* menu.

2.   Select the *Longitudinal Dispersivity* button.

3.   Select the *Constant -> Grid* button.

4.   Enter a value of 10.0 and select *OK*.

5.   Select the *OK* button to exit the *Longitudinal Dispersivity* dialog.

6.   Enter a value of 0.3 for the *Ratio of the trans. dispersivity to long. dispersivity* value.

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

2.6.6   The Source/Sink Mixing Package

Next, we will initialize the Source/Sink Mixing package and define the concentration at the spill location.

1.   Select the *Source/Sink Mixing Package* command in the *MT3D* menu.

2.   In the *Initialize Point Source/Sinks from MODFLOW* section in the lower right corner of the dialog, select the *Well* button.

At this point, the concentrations at the well can be edited directly from this dialog or by exiting the dialog, selecting the cell containing the well and selecting the *Point Source/Sink* command. Since there is only one well, the easiest approach in this case is to edit the concentration in this dialog. We will assign a concentration of 1000 mg/L for the BTEX and leave the oxygen at the default value of 0.0.

1.   Using the horizontal scroll bar below the spreadsheet section, scroll over until the BTEX column is visible.

2.   Change the BTEX value to 1000.0.

3. Select the *OK* button to exit the *Source/Sink Mixing Package* dialog.

2.6.7   The Chemical Reactions Package

The final step is to initialize the data for the Chemical Reactions package. In this case, the default values are adequate and no changes are necessary.

2.6.8   Running RT3D

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

1. Select the *Save As* command from the *MT3D* menu.

2. In the *Save As* dialog, check to make sure the path is still set to *tutorial\rt3d\btexins1*.

3. Enter "btexmod" for the file name.

4. Select the *Save* button.

To run RT3D:

1. Select the *Run RT3D* command from the *MT3D* menu.

2. Select *OK* at the prompt.

3. When the simulation is finished, return to GMS.

2.6.9   Viewing the Results

Now, we will read in the concentration files and view the results.

1. Select the *Read Solution* command from the *MT3D* menu.

2. Select *OK* at the prompt.

The contours you see are for Oxygen at the end of the first time step (73.0 days). To view the Oxygen solution at 730 days.

Select the 730.0 time step in the *TS* combo box at the upper right corner of the GMS window

To get a better plot of the concentration contours:

1. Select the *Contour Options* command in the *Data* menu.

2. Select the *Color fill between contours* option in the *Contour Method* section of the dialog.

3. Select the *Color Ramp Options* button.

4. Select the *Show color legend* option.

5. Select the *OK* button to exit the *Color Ramp Options* dialog.

6. Select the *OK* button to exit the *Contour Options* dialog.

Next, we will view the BTEX solution at 730 days.

Select the *BTEX* item in the *Data Set* combo box at the top of the GMS window

You may wish to use the *Data Set* and *TS* combo boxes to view the solution at other time steps.

2.6.10   Viewing a Film Loop Animation

The most effective post-processing tool for transient data is a film loop animation. We will set up a film loop showing the fate of the BTEX through the entire duration of the simulation.

To set up the film loop:

1. Select the *Film Loop* command in the *Data* menu.

2. Select the *Setup* button.

3. Turn on the *Display clock* option in the lower right corner of the dialog.

4. Select the *OK* button.

When the hourglass cursor disappears:

1. Select the *Play* button to begin the animation.

2. After viewing the animation, select the *Stop* button to stop the animation.

3. Select the *Step* button to move the animation one frame at a time.

4. You may wish to experiment with some of the other playback controls. When you are finished, select the *Done* button to exit the *Film Loop* dialog.

2.7   Conclusion

This concludes the *Instantaneous Aerobic Degradation* tutorial. If you wish to exit GMS at this time:

1. Select the *Exit* command from the *File* menu.

2. Select the *No* button at the prompt.

CHAPTER 3

BTEX Degradation with Multiple Electron Acceptors

This tutorial illustrates the steps involved in using GMS and RT3D to model BTEX degradation using a multiple electron acceptor model. Since the flow model used in this simulation is similar to the flow model used in *Chapter 2 - Instantaneous Aerobic Degradation*, the steps involved in building the flow model will not be described in this tutorial. A pre-defined version of the flow model will be used.

3.1   Description of the Reaction Model

The reaction we will be simulating is biodegradation of BTEX compounds via different aerobic/anaerobic pathways using multiple electron acceptors. Five different processes considered in this model are Aerobic Respiration (AR), Denitrification (DN), Iron (III) Reduction (IR), Sulfate Reduction (SR), and Methanogenesis (MG). All of these biochemical reactions are assumed to occur in the aqueous phase, mediated by the existing subsurface microbes, and are expected to happen in the following sequence:

$$AR \rightarrow DN \rightarrow IR \rightarrow SR \rightarrow MG \ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (3.1)$$

The following reaction kinetic framework is used to model the degradation rate of hydrocarbon via different electron acceptor pathways:

$$r_{HC,O_2} = -k_{HC,O_2}[HC]\frac{[O_2]}{K_{O_2}+[O_2]}$$ ....(3.2)

$$r_{HC,NO_3} = -k_{HC,NO_3}[HC]\frac{[NO_3]}{K_{NO_3}+[NO_3]} \bullet \frac{K_{i,O_2}}{K_{i,O_2}+[O_2]}$$ ....(3.3)

$$r_{HC,FE^{3+}} = -k_{HC,Fe^{3+}}[HC]\frac{[Fe^{3+}]}{K_{Fe^{3+}}+[Fe^{3+}]} \bullet \frac{K_{i,O_2}}{K_{i,O_2}+[O_2]}$$
$$\bullet \frac{K_{i,NO_3}}{K_{i,NO_3}+[NO_3]}$$ ....(3.4)

$$r_{HC,SO_4} = -k_{HC,SO_4}[HC]\frac{[SO_4]}{K_{SO_4}+[SO_4]} \bullet \frac{K_{i,O_2}}{K_{i,O_2}+[O_2]}$$
$$\bullet \frac{K_{i,NO_3}}{K_{i,NO_3}+[NO_3]} \bullet \frac{K_{i,Fe^{3+}}}{K_{i,Fe^{3+}}+[Fe^{3+}]}$$ ....(3.5)

$$r_{HC,CH_4} = -k_{HC,CH_4}[HC]\frac{[CO_2]}{K_{CH_4}+[CO_2]} \bullet \frac{K_{i,O_2}}{K_{i,O_2}+[O_2]}$$
$$\bullet \frac{K_{i,NO_3}}{K_{i,NO_3}+[NO_3]} \bullet \frac{K_{i,Fe^{3+}}}{K_{i,Fe^{3+}}+[Fe^{3+}]} \bullet \frac{K_{i,SO_4}}{K_{i,SO_4}+[SO_4]}$$ ....(3.6)

where $r_{HC,O2}$ is the rate at which hydrocarbon is destroyed by utilizing oxygen, $r_{HC,NO3}$ is the rate at which hydrocarbon is destroyed by utilizing Nitrate, $r_{HC,Fe2+}$ is the rate at which hydrocarbon is destroyed by producing Fe^{2+} (or utilizing Fe^{3+}), $r_{HC,SO4}$ is the rate at which hydrocarbon is destroyed by utilizing sulfate, $r_{HC,CH4}$ is the rate at which hydrocarbon is destroyed by producing methane, $[O_2]$ is the oxygen concentration $[ML^{-3}]$, k_{O2} is the first-order rate constant $[T^{-1}]$, K_{O2} is the Monod half saturation constant $[ML^{-3}]$ (by setting all the half-saturation constants to a small value we can simulate zero-order dependency with respect to the electron donor and hence a first-order degradation model with respect to hydrocarbon; the default values simulate this option), and $K_{i,o2}$ is the oxygen inhibition constant $[ML^{-3}]$ (by setting all inhibition constants to a small value we can force the reactions to occur in a sequential fashion; the default values simulate this process). Similar nomenclature is used to identify other Monod constants and inhibition coefficients.

Since the concentrations of Fe^{3+} and CO_2 are not readily measurable under normal field conditions, these terms were replaced with the "assimilative capacity" for iron reduction and methanogenesis, defined as:

$$[Fe^{3+}] = [Fe^{2+}{}_{max}] - [Fe^{2+}] \quad\text{...} (3.7)$$

$$[MC] = [CO_2] = [CH_{4,max}] - [CH_4] \quad\text{...} (3.8)$$

where $[Fe^{2+}{}_{max}]$ and $[CH_{4\ max}]$ are the maximum possible aquifer levels of these species that represent the aquifer's maximum capacity for iron reduction and methanogenesis. Note, the concentration of CO_2 used here is the CO_2 evolved while the hydrocarbon is destroyed via methanogenesis which may be thought of as the "Methanogenic Capacity" (MC) of the aquifer. Using these relations, iron (III) reduction and methanogenesis processes may be related back to measurable Fe^{2+} and CH_4 concentration levels.

The total rate of hydrocarbon destruction, via all the above described processes, is the sum of each of the individual rates and is given as:

$$\frac{d[HC]}{dt} = r_{HC,O_2} + r_{HC,NO_3} + r_{HC,Fe^{2+}} + r_{HC,SO_4} + r_{HC,CH_4} \quad\text{.........................} (3.9)$$

Rates of electron acceptor utilization are given as the corresponding rate of hydrocarbon destruction multiplied by the appropriate yield coefficient (Y):

$$\frac{d[O_2]}{dt} = Y_{O_2/HC}\, r_{HC,O_2} \quad\text{...} (3.10)$$

$$\frac{d[NO_3]}{dt} = Y_{NO_3/HC}\, r_{HC,NO_3} \quad\text{...} (3.11)$$

$$\frac{d[Fe^{2+}]}{dt} = -Y_{Fe^{2+}/HC}\, r_{HC,Fe^{2+}} \quad\text{...} (3.12)$$

$$\frac{d[SO_4]}{dt} = Y_{SO_4/HC}\, r_{HC,SO_4} \quad\text{...} (3.13)$$

$$\frac{d[CH_4]}{dt} = -Y_{CH_4/HC}\, r_{HC,CH_4} \quad\text{...} (3.14)$$

The yield values (the mass ratio of electron acceptors removed or metabolic byproducts produced to total BTEX degraded) are: $Y_{02/HC} = 3.14$, $Y_{NO3/HC} = 4.9$, $Y_{Fe2+/HC} = 21.8$, $Y_{SO4/HC} = 4.7$, and $Y_{CH4/HC} = 0.78$. Typical values of all inhibition coefficients, except for $KiFe^{3+}$, should be in the range of 1.0 to 0.01 mg/L. $KiFe^{3+}$ should always be set around 40% to 80% of the max Fe^{2+} value. Monod half-saturation constants should be in the range of 1.0 to 0.1 mg/L.

As pointed out in Lu et al. (G. Lu, T.P. Clement, C. Zheng, and T.H. Wiedemeier, Natural attenuation of BTEX compounds: model development and field-scale application, Ground Water, vol.37(5), p.707-717, 1999), it is important to note that this model is based on several assumptions. The model should be used with caution only at sites where these assumptions are valid. In summary, the key assumptions used in the model are: (1) the fuel chemical species benzene, toluene, ethylbenzene, and xylene are assumed to degrade at similar rates, and hence are combined and modeled as a single electron donor species BTEX; (2) production of Fe^{2+} and methane are restricted at a node to a "maximum-observed level"; however, the model assumes that an infinite supply of electron acceptors will be available for iron-reduction and methanogenic reactions; (3) more complex processes such as the rate-limited interaction of bioavailable, solid-phase Fe^{3+} and aqueous-phase Fe^{+2}, interaction of oxygen and Fe2+, and/or variations in the spatial pattern of methanogenic activity and CO_2 availability are not considered; (4) growth and decay of various microbial populations and their interactions with contaminants and aquifer solids are assumed to be negligible; (5) all BTEX decay reactions are approximated as first-order reactions and hence the model ignores the Monod limitation due to the electron donor (BTEX) availability. Fortunately, these assumptions are expected to be reasonable approximations for most field sites. However, there will always be some exceptions.

3.2   Description of Problem

The problem we will be solving in this tutorial is similar to the problem described in the first tutorial (Figure 2.1). The site is a 510 m X 310 m section of a confined aquifer with a flow gradient from left to right. An underground storage tank is leaking fuel hydrocarbon contaminants at 2 m^3/day at the location shown. Concentration of BTEX is 1000 mg/L. Initial levels of hydrocarbon, oxygen, nitrate, Fe^{2+}, sulfate, and methane in the aquifer are assumed to be: 0.0, 4.0, 20.0, 0.0, 10.0, and 0.0 mg/L, respectively. The reaction constants to be used are as follows:

Constant	Value
Max Fe2+	25.0 mg/L
Max Methane	30.0 mg/L
$k_{HC,O2}$	0.1 day^{-1}
$k_{HC,No3}$	0.008 day^{-1}
$k_{HC,Fe3+}$	0.0005 day^{-1}
$k_{HC,SO4}$	0.00025 day^{-1}
$k_{HC,CH4}$	0.0001 day^{-1}

Values of all inhibition coefficients, except KiFe3+, are assumed to be 0.01 mg/L and all Monod constants are assumed to 0.5 mg/L. The value of KieFe3+ is set at 12.5 mg/L (50% of max Fe). The yield values are the same as those described in the previous section.

The first part of the problem will be to import a previously computed MODFLOW flow model of the site. Using this flow field, a reactive transport model will then be defined using RT3D.

3.3   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.

3.4   Required Modules/Interfaces

This tutorial utilizes the following components of the GMS interface:

- The *3D Grid* module
- The MODFLOW interface
- The RT3D interface

You can confirm whether each of these components has been enabled on your copy of GMS by selecting the *Register* command from the *File* menu. If you have licensed and enabled each of the listed items on your version of GMS, you can proceed to complete the tutorial in normal mode. If not, you will need to obtain an updated password or hardware lock before continuing.

3.5   Importing the MODFLOW Model

The first part of the simulation is to import the MODFLOW flow model. A steady state flow model has been previously computed and is supplied with the tutorial files.

1. Switch to the *3D Grid Module*
2. Select the *Read Simulation* command in the *MODFLOW* menu.
3. In the *Open* dialog, locate and open the file entitled *tutorial\rt3d\flowmod\flowmod1.mfs*.

3.6   Building the Transport Model

Now that the flow model is imported, the next step is to set up the RT3D simulation. For this part of the simulation, we will select the reaction, define the reaction data, define the supplemental layer data needed by RT3D, and assign concentrations to the well.

3.7   Initializing the Model

The first step is to initialize the RT3D data.

Select the *New Simulation* command in the *MT3D* menu.

3.8   The BTN Package

The next step is to initialize the data in the *Basic Transport Package*. First, we will initialize the data, select RT3D as the transport model, and select the appropriate packages.

1.   Select the *Basic Transport Package* command from the *MT3D* menu.

2.   Select the *RT3D* option.

3.   Select the *Packages* button.

4.   Select the *Advection Package*, the *Dispersion Package*, the *Source/Sink Mixing Package*, and the *Chemical Reaction Package*.

5.   For the *RT3D reactions*, select the *Kinetic-Limited Deg. of BTEX w/ MEA* option.

6.   Select the *OK* button to exit the *Packages* dialog.

3.8.1   Starting Concentrations

Note that in the *Starting Concentration* section of the dialog, the species associated with the reaction we are modeling are listed by name. The next step is to define the starting concentration for each of these species. The default starting concentration is zero. We will use the default value for BTEX, Fe^{2+}, and methane, but we will use non-zero values for oxygen (4.0 mg/L), nitrate (20.0 mg/L), and sulfate (10.0 mg/L).

1.   Select *Oxygen* from the list of species.

2.   Select the *Starting Concentration* button.

3.   Select the *Constant -> Grid* button.

4.   Enter a value of 4.0.

5.   Select the *OK* button.

6.   Select the *OK* button to exit the *Starting Concentration* dialog.

7. Repeat these steps to enter a starting value of 20.0 for the nitrate and 10.0 for the sulfate.

3.8.2   Porosity

Next, we will define the porosity.

1. Select the *Porosity* button.

2. Select the *Constant -> Grid* button.

3. Enter a value of 0.3 and select *OK*.

4. Select the *OK* button to exit the *Porosity* dialog.

3.8.3   Stress Periods

Next, we will define the stress periods. Since the injection rate and the boundary conditions do not change, we will use a single stress period with a length of 730 days (two years).

1. Select the *Stress Periods* button.

2. Enter a value of 730 for the *Length*.

3. Enter a value of 10 for the *No. of time steps*.

4. Select the *OK* button to exit the *Stress Periods* dialog.

3.8.4   Output Options

Finally, we will define the output options. One binary solution file is created by RT3D for each of the species. By default, RT3D saves a solution at each transport step for each species. Since this results in large files containing more solutions than we need for the simple post-processing we intend to do, we will specify that a solution be saved every 73 days (every time step).

1. Select the *Output Control* button.

2. Select the *Print at specified times* option.

3. Select the *Times* button.

4. Select the *Initialize Values* button.

5. Enter 73.0 for the *Initial time step size*.

6. Enter 73.0 for the *Maximum time step size*.

7. Enter 730.0 for the *Maximum simulation time*.

8. Select the *OK* button to exit the *Initialize Time Steps* dialog.

9. Select the *Close* button to exit the *Variable Time Steps* dialog.

10. Select the *Close* button to exit the *Output Control* dialog.

This completes the input for the Basic Transport package.

Select the *Close* button to exit the *Basic Transport Package* dialog.

3.9   Assigning Concentrations to the Left Boundary

The left boundary of the model is a constant head boundary. Since the head at the left boundary is greater than the head at the right boundary, the left boundary acts as a source and water enters the model from the left. Thus, we must define the concentrations of our species at the left boundary. The simplest way to do this is to mark the cells as specified concentration cells.

1. Select the *Select Cell* tool

2. Select the cells on the left boundary by dragging a box that just surrounds the cells.

3. Select the *Cell Attributes* command in the *MT3D* menu.

4. Change the *ICBUND* value to −1.

5. Select the *OK* button.

3.10   The Advection Package

The next step is to initialize the data for the Advection package.

1. Select the *Advection Package* command from the *MT3D* menu.

2. Select the *Standard finite-difference method* solver from *the Solution Scheme* section of the dialog.

3. Select the *OK* button.

3.11   The Dispersion Package

Next, we will enter the data for the Dispersion package. The aquifer has a longitudinal dispersivity of 10.0 m and a transverse (horizontal) dispersivity of 3.0 m.   The vertical dispersivity is assumed to be equal to the longitudinal dispersivity.

1. Select the *Dispersion Package* command in the *MT3D* menu.

2. Select the *Longitudinal Dispersivity* button.

3. Select the *Constant -> Grid* button.

4. Enter a value of 10.0 and select *OK*.

5. Select the *OK* button to exit the *Longitudinal Dispersivity* dialog.

6. Enter a value of 0.3 for the *Ratio of the transverse dispersivity to long. dispersivity* value.

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

3.12   The Source/Sink Mixing Package

Next, we will initialize the Source/Sink Mixing package and define the concentration at the spill location. We will assign a concentration of 1000 mg/L for BTEX and leave the other electron acceptor concentrations at the default value of zero.

1. Select the *Source/Sink Mixing Package* command in the *MT3D* menu.

2. In the *Initialize Point Sources/Sinks from MODFLOW* section in the lower right corner of the dialog, select the *Well* button.

3. Using the horizontal scroll bar below the spreadsheet section, scroll over until the BTEX column is visible.

4. Change the BTEX value to 1000.0.

5. Select the *OK* button to exit the *Source/Sink Mixing Package* dialog.

3.13   The Chemical Reaction Package

Next, we will initialize the Chemical Reaction package and define appropriate reaction rate constants.

1. Select the *Chemical Reaction Package* command in the *MT3D* menu.

2. In the *Reaction Parameters* section, click on the *Max Fe2+* item and set its value to 25.0.

3. Likewise, set the value of *Max Methane* to 30.0.

4. Set the value of $k_{HC,O2}$ to 0.1.

5. Set the value of $k_{HC,NO3}$ to 0.008.

6. Set the value of $k_{HC,Fe3+}$ to 0.0005.

7. Set the value of $k_{HC,SO4}$ to 0.00025.

8. Set the value of $k_{HC,CH4}$ to 0.0001.

All monod constants inhibition coefficients, and yield values, except KiFe3+, will be left at the default values. The value of KiFe3+ is set at 12.5 mg/L (50% of max Fe).

9. Set the value of KiFe3+ to 12.5.

10. Select the OK button.

3.14   Running RT3D

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

1. Select the *Save As* command from the *MT3D* menu.

2. In the *Save As* dialog, locate and open the directory entitled *tutorial\rt3d\btexkin*.

3. Enter "btmod" for the file name.

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

To run RT3D:

1. Select the *Run RT3D* command from the *MT3D* menu.

2. Select *OK* at the prompt.

3. When the simulation is finished, close the window and return to GMS.

3.15   Viewing the Results

Now, we will read in the concentration files and view the results.

1. Select the *Read Solution* command from the *MT3D* menu.

2. Select *OK* at the prompt.

First, we will view the BTEX solution at 730 days.

1. Select the *BTEX* data set from the *Data Set* combo box at the top of the GMS window.

2. Select the time step at 730 days from the *TS* combo box at the top of the GMS window.

3.15.1 Overlaying Contours

Next, we will view concentration contours for the other species. When working with multiple species, it is often convenient to overlay contours of one species on top of contours from another species. As an example, we will overlay the contours of the other species on top of the BTEX contours. To do this, we must save a copy of the BTEX contours to a DXF file, read the file in, and display the BTEX contours in the background.

Before saving the DXF file, we will turn off most of the display options other than the contours (to avoid saving the grid cell lines to the DXF file).

1. Select the *Display Options* command in the *Display* menu.

2. Turn off the *Cells* option.

3. Select the *OK* button.

To save the contours to a DXF file:

1. Select the *Export* command in the *File* menu.

2. Change the file filter to *DXF Files (*.dxf)*.

3. Enter "btexcont.dxf" for the file name.

4. Select the *Save* button.

Before reading the contours back in, we will reset the display options and view the oxygen solution at 730 days.

1. Select the *Display Options* command in the *Display* menu.

2. Turn on the *Layer Boundaries* option.

3. Select the *OK* button.

4. Select the *Oxygen* data set from the *Data Set* combo box at the top of the GMS window.

We will also turn on a color ramp and a legend.

1. Select the *Contour Options* command in the *Data* menu.

2. Select the *Use color ramp* option.

3. Select the *Color Ramp Options* button.

4. Select the *Show color legend* option.

5. Select the *OK* button to exit the *Color Ramp Options* dialog.

6. Select the *OK* button to exit the *Contour Options* dialog.

Now we are ready to import the BTEX contours.

1. Select the *Import* command in the *File* menu.

5. Change the file filter to *DXF Files (*.dxf)*.

2. Select and open the "btexcont.dxf" file.

Next, we will view the nitrate solution at 730 days.

Select the *Nitrate* data set from the *Data Set* combo box at the top of the GMS window.

Finally, we will view the Fe^{2+} solution at 730 days.

Select the *Iron(Fe2+)* data set from the *Data Set* combo box at the top of the GMS window.

3.15.2 Other Post-Processing Options

At this point, you may wish to experiment with the other post-processing options, including film loop animation.

3.16   Conclusion

This concludes the tutorial: *BTEX Degradation with Multiple Electron Acceptors*. If you wish to exit GMS at this time:

1. Select the *Exit* command from the *File* menu.

2. Select the *No* button at the prompt.

CHAPTER   4

Sequential Anaerobic Degradation: PCE→TCE→DCE→VC

This tutorial illustrates the steps involved in modeling sequential anaerobic degradation of PCE using the RT3D model. Since the flow model used in this simulation is similar to the flow model used in *Chapter 2 - Instantaneous Aerobic Degradation*, the steps involved in building the flow model will not be described in this tutorial. A pre-defined version of the flow model will be used.

4.1   Description of Problem

The problem we will be solving in this tutorial is similar to the problem described in the first tutorial (Figure 2.1). The site is a 510 m X 310 m section of a confined aquifer with a flow gradient from left to right. An underground storage tank is leaking fuel hydrocarbon contaminants at 2 m³/day at the location shown. Concentration of PCE is 1000 mg/L. This high hypothetical concentration was selected to simulate a plume (with considerable PCE mass) with a relatively low injection flow rate. Details of the aquifer hydrology and geometry are shown in Figure 2.1. Initial levels of PCE and its degradation products in the aquifer are assumed to be 0.0 mg/L. We will simulate a continuous spill event and compute the resulting PCE, TCE, DCE and VC contours after three years.

The first part of the problem will be to import a previously computed MODFLOW flow model of the site. Using this flow field, a reactive transport model will then be defined using RT3D.

4.2   Description of Reaction

The reaction we will be simulating is anaerobic PCE dechlorination with sequential, first-order, degradation kinetics. Degradation of PCE all the way to VC is assumed to anaerobically favorable and the degradation kinetics are assumed to be first-order in nature.

$$PCE \rightarrow TCE \rightarrow DCE \longrightarrow VC \qquad \dotfill (4.1)$$

The following set of equations describes the reaction kinetics framework.

$$r_{PCE} = -k_1[PCE] \qquad \dotfill (4.2)$$

$$r_{TCE} = k_1 Y_{TCE/PCE}[PCE] - k_2[TCE] \qquad \dotfill (4.3)$$

$$r_{DCE} = k_2 Y_{DCE/TCE}[TCE] - k_3[DCE] \qquad \dotfill (4.4)$$

$$r_{DCE} = k_3 Y_{VC/DCE}[DCE] - k_4[VC] \qquad \dotfill (4.5)$$

Kinetic Constants (to be input by the user):

Constant	Value	Designation
k_1	0.005 day^{-1}	PCE anaerobic constant
k_2	0.003 day^{-1}	TCE anaerobic constant
k_3	0.002 day^{-1}	DCE anaerobic constant
k_4	0.001 day^{-1}	VC anaerobic constant

The following constants (yields in mg/mg basis) are fixed internally:

Constant	Value	Designation
$Y_{TCE/PCE}$	0.7920	TCE:PCE stoichiometric yield
$Y_{DCE/TCE}$	0.7377	DCE:TCE stoichiometric yield
$Y_{VC/DCE}$	0.6445	VC:DCE stoichiometric yield

4.3   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.

4.4   Required Modules/Interfaces

This tutorial utilizes the following components of the GMS interface:

- The *3D Grid* module
- The MODFLOW interface
- The RT3D interface

You can confirm whether each of these components has been enabled on your copy of GMS by selecting the *Register* command from the *File* menu. If you have licensed and enabled each of the listed items on your version of GMS, you can proceed to complete the tutorial in normal mode. If not, you will need to obtain an updated password or hardware lock before continuing.

4.5   Importing the MODFLOW Model

The first part of the simulation is to import the MODFLOW flow model. A steady state flow model has been previously computed and is supplied with the tutorial files.

1.   Switch to the *3D Grid Module.*

2.   Select the *Read Simulation* command in the *MODFLOW* menu.

3.   In the *Open* dialog, locate and open the file entitled *tutorial\rt3d\flowmod\flowmod1.mfs*.

At this point, you should see a grid appear.

4.6   Building the Transport Model

Now that the flow model is imported, the next step is to perform the RT3D simulation. For this part of the simulation, we will select the reaction, define the reaction data, define the supplemental layer data needed by RT3D, and assign concentrations to the well.

4.7   Initializing the Model

The first step is to initialize the RT3D data.

Select the *New Simulation* command in the *MT3D* menu.

4.8   The BTN Package

The next step is to initialize the data in the Basic Transport Package. First, we select RT3D as the transport model, and select the appropriate packages.

1.   Select the *Basic Transport Package* command from the *MT3D* menu.

2.   Select the *RT3D* option.

3. Select the *Packages* button.

4. Select the *Advection Package*, the *Dispersion Package*, the *Source/Sink Mixing Package*, and the *Chemical Reaction Package*.

5. For the *RT3D reactions*, select the *Sequential Decay Reactions* option.

6. Select the *OK* button to exit the *Packages* dialog.

4.8.1   Starting Concentrations

Note that in the *Starting Concentration* section of the dialog, the species associated with the reaction we are modeling are listed by name. The next step is to define the starting concentration for each of these species. By default all of the starting concentrations are zero. Since the aquifer is assumed to be initially clean, we will simply accept the default values for starting concentrations.

4.8.2   Porosity

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

4.8.3   Stress Periods

Next, we will define the stress periods. Since the injection rate and the boundary conditions do not change, we will use a single stress period with a length of 730 days (two years).

5. Select the *Stress Periods* button.

6. Enter a value of 730 for the *Length*.

7. Enter a value of 10 for the *No. of time steps*.

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

4.8.4   Output Options

Finally, we will define the output options. One binary solution file is created by RT3D for each of the species. By default, RT3D saves a solution at each transport step for each species. Since this results in large files containing more solutions than we need for the simple post-processing we intend to do, we will specify that a solution be saved every 73 days (every time step).

1. Select the *Output Control* button.

2. Select the *Print at specified times* button.

3. Select the *Times* button.

4. Select the *Initialize Values* button.

5. Enter 73.0 for the *Initial time step size*.

6. Enter 73.0 for the *Maximum time step size*.

7. Enter 730.0 for the *Maximum simulation time*.

8. Select the *OK* button to exit the *Initialize Time Steps* dialog

9. Select the *Close* button to exit the *Variable Time Steps* dialog.

10. Select the *Close* button to exit the *Output Control* dialog.

This completes the input for the Basic Transport package.

Select the *Close* button to exit the *Basic Transport Package* dialog.

4.9   The Advection Package

The next step is to initialize the data for the Advection package.

1. Select the *Advection Package* command from the *MT3D* menu.

2. Select the *Standard finite-difference method* solution scheme.

3. Select the *OK* button.

4.10   The Dispersion Package

Next, we will enter the data for the Dispersion package. The aquifer has a longitudinal dispersivity of 10.0 m and a transverse (horizontal) dispersivity of 3.0 m. The vertical dispersivity is not used since this is a one layer model.

1. Select the *Dispersion Package* command in the *MT3D* menu.

2. Select the *Longitudinal Dispersivity* button.

3. Select the *Constant -> Grid* button.

4. Enter a value of 10.0 and select *OK*.

5. Select the *OK* button to exit the *Longitudinal Dispersivity* dialog.

6.   Enter a value of 0.3 for the *Ratio of the transverse dispersivity to long. dispersivity* value.

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

4.11   The Source/Sink Mixing Package

Next, we will initialize the Source/Sink Mixing package and define the concentration at the spill location. We will assign a concentration of 1000 mg/L for PCE and leave TCE, DCE, and VC concentrations at the default value of 0.0

1.   Select the *Source/Sink Mixing Package* command in the *MT3D* menu.

2.   In the *Initialize Point Source/Sinks from MODFLOW* section in the lower right corner of the dialog, select the *Well* button.

3.   Using the horizontal scroll bar below the spreadsheet section, scroll over until the PCE column is visible.

4.   Change the PCE value to 1000.0.

5.   Select the *OK* button to exit the *Source/Sink Mixing Package* dialog.

4.12   The Chemical Reaction Package

Next, we will initialize the chemical reaction package and define appropriate reaction rate constants.

1.   Select the *Chemical Reaction Package* command in the *MT3D* menu.

2.   In the *Reaction Parameters* section, click on K_{pce} and set its value to 0.005.

3.   Likewise, set the value of K_{tce} to 0.003.

4.   Set the value of K_{dce} to 0.002.

5.   Set the value of K_{vc} to 0.001.

6.   Select the *OK* button.

4.13   Running RT3D

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

1. Select the *Save As* command from the *MT3D* menu.

2. In the *Save As* dialog, locate and open the directory entitled *tutorial\rt3d\pce1*.

3. Enter "rtmod" for the file name.

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

To run RT3D:

1. Select the *Run RT3D* command from the *MT3D* menu.

2. Select *OK* at the prompt.

3. When the simulation is finished, close the window and return to GMS.

4.14   Viewing the Results

Now, we will read in the concentration files and view the results.

1. Select the *Read Solution* command from the *MT3D* menu.

2. Select *OK* at the prompt.

First, we will view the PCE solution at 730 days.

1. Select the *PCE* data set from the *Data Set* combo box at the top of the GMS window.

2. Select the *730.0* time step from the *TS* combo box at the top of the GMS window.

To view color-fill contours:

1. Select the *Contour Options* command in the *Data* menu.

2. Select the *Color fill between contours* option.

3. Select the *Color Ramp Options* button.

4. Select the *Show color legend* option.

5. Select the *OK* button to exit the *Color Ramp Options* dialog.

6. Select the *OK* button to exit the *Contour Options* dialog.

Next, we will view the other solutions at 730 days.

1. Select the *TCE* data set from the *Data Set* combo box at the top of the GMS window

2. Select the *DCE* data set from the *Data Set* combo box at the top of the GMS window

3. Select the *VC* data set from the *Data Set* combo box at the top of the GMS window

4.14.1 Creating a Time Series Plot

Another highly effective tool for viewing RT3D solutions is a time series plot. A time series plot is used to display the variation of concentration vs. time for one or more species at a particular point in the model. Time series plots are set up using an observation coverage in the *Map* module.

First, we will define an observation coverage.

1. Switch to the *Map* module

2. Select the *Coverages* command in the *Feature Objects* menu.

3. In the *Coverage type* combo box, select the *Observation* option.

4. Select the *OK* button to exit the *Coverages* dialog.

Next, we will create an observation point.

1. Select the *Create Point* tool

2. Click on a point somewhere in the grid downgradient of the well.

The final step is to create a time series plot.

1. Select the *Obs. Plot Options* command in the *Display* menu.

2. Select the *New* button to create a new plot.

3. In the *Plot type* combo box, select the *Time series* option.

4. Select the *OK* button.

5. Select the *Show Plot Window* command in the *Display* menu.

Moving the Observation Point

At this point, you should see a plot of the active data set (VC) vs. time. The plot can easily be changed to display the variation in the data set at a different location.

1. Select the *Select Point/Node* tool

2. Click on the observation point and drag it to a new location (Note: you may need to reposition or resize the *Plot Window* to see the observation point).

Plotting Multiple Data Sets

By default, only the active data set is plotted. For RT3D solutions, it is often useful to include all of the species in the plot. This can be accomplished as follows:

1. Select the *Obs. Plot Options* command in the *Display* menu.

2. Select the *Options* button.

3. Select the *Use selected data set* option.

4. In the list of data sets, select each of the data sets that are not displayed and turn on the *Display* toggle.

5. Select the *OK* button to exit the *Time Series Plot Options* dialog.

6. Turn on the *Curve legend* option (this will help us distinguish which data set goes with which curve).

7. Select the *OK* button to exit the *Observation Plot Options* dialog.

8. Reselect the observation point if necessary.

Once again, note that you can move the point anywhere in the grid and the plot is updated.

4.14.2   Other Post-Processing Options

At this point, you may wish to experiment with the other post-processing options, including film loop animation.

4.15   Conclusion

This concludes the tutorial: *Sequential Anaerobic Degradation: PCE->TCE->DCE->VC*. If you wish to exit GMS at this time:

1. Select the *Exit* command from the *File* menu.

2. Select the *NO* button at the prompt.

CHAPTER 5

User-Defined Reactions

The objective of this chapter is to describe the steps involved in developing a user defined reaction module for simulating reactions that can not be simulated using a pre-defined RT3D-reaction package. Once developed, users can distribute the new reaction package to other interested modelers for applying the reaction model at different sites (i.e., it can be treated like a pre-defined reaction package). Note that RT3D (version 2 beta) has an option to support a new reaction solver that uses Jacobian matrices. However, this option will not be discussed in this example. Interested users should refer to the RT3D (version 2 beta) update document.

5.1   Steps Involved in Creating a User-Defined Reaction

User-defined reaction packages can be created using one of two approaches: the dynamically linked library (DLL) option or the linked subroutine option. With the DLL option, the subroutine for the reaction package is compiled as a stand-alone DLL. The DLL is then copied to the same directory as the RT3D executable and the DLL is automatically launched by RT3D when RT3D is executed. The DLL can be recompiled or a new DLL can be used simply by copying the new DLL to the same directory as the RT3D executable and naming it appropriately. The RT3D executable does not need to be recompiled.

With the linked subroutine option, the code for the new reaction subroutine is compiled and linked with the rest of the RT3D source code (or the RT3D library made for a specific computer platform). In other words, the RT3D executable must be recompiled each time the reaction package is modified.

Because of the portability of the developed reaction package, the DLL option is the more convenient of the two options. However, the DLL option is only available on the *Windows 95/98/NT* platform. It is not available on *Unix*.

This tutorial describes the DLL approach for creating user-defined reaction packages. Special instructions for the *Unix* platform are contained in Section 5.16 on page 5-20.

5.2 Required Background

As a reaction module developer, you are considered an advanced user of the RT3D code. The required background is as follows:

- Should have a basic understanding of the functionality of RT3D code and understand how different types of components (mobile and immobile) are mathematically described within RT3D-modeling framework.

- Should be familiar with GMS 3.1 and be able to create MODFLOW and RT3D input files with little effort.

- Should be familiar with the data structure of RT3D input files such as BTN, SSM, and RCT files.

- Should have a basic understanding of the FORTRAN language, and have access to A Digital FORTRAN compiler (or a UNIX system based FORTRAN 90 compiler).

- Should have some background/understanding of biochemical reaction kinetics. Note inappropriate kinetic expressions and/or kinetic constants may lead to unpredictable code behavior.

- Should be familiar with contaminant transport equations, and coupled nonlinear differential equations.

5.3 Reaction Module Description

The flow and transport model we will be developing in this tutorial exercise is identical to the one described in the tutorial entitled: *Sequential Anaerobic Degradation: PCE->TCE->DCE->VC*.

Assuming first-order sequential biodegradation kinetics, the transformation of PCE and its decay products, along with its transport, can be predicted using the following set of partial differential equations:

$$R_P \frac{\partial[PCE]}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial[PCE]}{\partial x_j}\right) - \frac{\partial(v_i[PCE])}{\partial x_i} + \frac{q_s}{\phi}[PCE]_s - K_{PCE}[PCE]$$

$$R_T \frac{\partial[TCE]}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial[TCE]}{\partial x_j}\right) - \frac{\partial(v_i[TCE])}{\partial x_i} + \frac{q_s}{\phi}[TCE]_s + Y_{Tce/Pce}K_{Pce}[PCE] - K_{Tce}[TCE]$$

$$R_D \frac{\partial[DCE]}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial[DCE]}{\partial x_j}\right) - \frac{\partial(v_i[DCE])}{\partial x_i} + \frac{q_s}{\phi}[DCE]_s + Y_{Dce/Tce}K_{Tce}[TCE] - K_{Dce}[DCE]$$

$$R_V \frac{\partial[VC]}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial[VC]}{\partial x_j}\right) - \frac{\partial(v_i[VC])}{\partial x_i} + \frac{q_s}{\phi}[VC]_s + Y_{Vc/Dce}K_{Dce}[DCE] - K_{Vc}[VC]$$

where [PCE], [TCE], [DCE], and [VC] are the concentrations of the respective contaminants in mg/L; K_{PCE}, K_{TCE}, K_{DCE}, and K_{VC} are first-order degradation rates, R_P, R_T, R_D, R_V are retardation coefficients; and $Y_{TCE/PCE}$, $Y_{DCE/TCE}$, and $Y_{VC/DCE}$ are yield coefficients whose values can be computed from stoichiometric relations as 0.79, 0.74, and 0.64, respectively [for example, based the chemical reaction stochiometry, one mole of PCE will yield one mole of TCE (or 165.8 grams of PCE will yield 131.36 grams of TCE), therefore the yield value for $Y_{TCE/PCE} = 131.36/165.8 = 0.79$].   The kinetic model formulation presented assumes that the biological degradation reactions occur only in the liquid phase (a more conservative assumption).

Using the reaction operator-split strategy, the biological reaction kinetics can be separated from the transport equations and assembled together into a set differential equations:

$$\frac{d[PCE]}{dt} = -\frac{K_{Pce}[PCE]}{R_P}$$

$$\frac{d[TCE]}{dt} = \frac{Y_{Tce/Pce}K_{Pce}[PCE] - K_{Tce}[TCE]}{R_T}$$

$$\frac{d[DCE]}{dt} = \frac{Y_{Dce/Tce}K_{Tce}[TCE] - K_{Dce}[DCE]}{R_D}$$

$$\frac{d[VC]}{dt} = \frac{Y_{Vc/Dce}K_{Dce}[DCE] - K_{Vc}[VC]}{R_V}$$

The above set of coupled differential equations describes the kinetics of PCE degradation and its daughter products.

5.4   Coding a New Reaction Package

Three different methods can be used for coding a new user-defined reaction package. Each method treats the reaction parameter information (values of K_{tce}, K_{pce}, etc.) in a different fashion.

1. In the first method, all reaction parameter values are explicitly assigned within the reaction module prior to compilation. This is not an efficient method since it requires recompilation of the reaction routine whenever a reaction parameter value is modified. However, this method is recommended for testing a new reaction module with the BATCHRXN utility.

2. In the second method, all of the reaction parameter values are spatially constant but are assigned/modified externally, as input data, via the *.RCT file (to run RT3D) or batch.in file (to run BATCHRXN).

3. In the third method, some or all of the reaction parameters are treated as spatially variable (i.e. a different value may be assigned to each cell). The parameter values should be externally assigned/modified as input data, via the *.RCT file. This option should be used with caution because it may require significant computer resources, both execution time and memory!

We will first use method #1 in this tutorial; later, we will modify the code to demonstrate method #3.

5.4.1   Editing the Source Code of Reaction Module

The complete listing of the FORTRAN subroutine (using method-#1) that describes the PCE degradation reactions is given below:

```
SUBROUTINE rxns(ncomp,nvrxndata,j,i,k,y,dydt,
     &            poros,rhob,reta,rc,nlay,nrow,ncol,vrc)
c ***** Block 1: Comments block *******
c234567890123456789012345678901234567890123456789012345678901234567890123456789012
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 [array variable reta(mcomp)]
c rhob -  bulk density of the node
c rc - Stores spatially constant reaction parameters (up to 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: 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 First_time
      DATA First_time/1/
      DOUBLE PRECISION y,dydt,poros,rhob,reta
      DOUBLE PRECISION rc,vrc
      DIMENSION y(ncomp),dydt(ncomp),rc(50)
      DIMENSION vrc(ncol,nrow,nlay,nvrxndata),reta(50)
C ****** End of block 2 *******
```

```
C *** Block 3: Declare your problem-specific new variables here ***
C     INTEGER
      DOUBLE PRECISION pce,tce,dce,vc,kpce,ktce,kdce,kvc
      DOUBLE PRECISION ytcepce,ydcetce,yvcdce
C ***** End of Block 3  ******

C *** Block 4: Initilize reaction parameters here, if required ***
      IF (First_time .EQ. 1) THEN
          kpce = 0.005  !PCE first-order degradation rate
          ktce = 0.003  !TCE first-order degradation rate
          kdce = 0.002  !DCE first-order degradation rate
          kvc = 0.001   !VC first-order degradation rate
          ytcepce = 131.36/165.8
          ydcetce = 96.9/131.36
          yvcdce = 62.45/96.9
          First_time = 0 !reset First_time to skip this block later
      END IF
C ***** End of Block 4  ******

C  *** Block 5: Definition of other variable names ***
      pce = y(1)
      tce = y(2)
      dce = y(3)
      vc = y(4)
C ***** End of Block 5  ******

c  *** Block 6: Definition of Differential Equations ***
      dydt(1) = -kpce*pce/reta(1)
      dydt(2) = (-ktce*tce + kpce*pce*ytcepce)/reta(2)
      dydt(3) = (-kdce*dce + ktce*tce*ydcetce)/reta(3)
      dydt(4) = (-kvc*vc + kdce*dce*yvcdce)/reta(4)
C ***** End of Block 6  ******
      RETURN
      END
```

Note that the reaction subroutine listed above is organized into the following six distinct blocks of FORTRAN code:

1. The comment block

    This block contains a definition for all the variables that are passed into the rxns routine from the RT3D main program.

2. The interfacing block

    This block contains FORTRAN statements that define the type of passed variables. This block should not be altered under any circumstances.

3. The local variable definition block

    This block is used define all the new local variables that are used exclusively in the rxns subroutine.

4. The reaction parameter initialization block

    This block is used to specify values for all the reaction parameters (such as K_{TCE}, K_{PCE}, etc.). Note that this initialization block is executed only when the subroutine is called for the first time.

5. Variables naming block

This block is typically used to transfer certain passed variables into meaningful names (this is required for code clarity purposes only).

6. The differential equations block

This block is used to describe the PCE degradation reaction equations in FORTRAN language.

The FORTRAN subroutine presented above is provided with the GMS files in the following location:

```
tutorial\rt3d\userdef\rxns_1.f
```

You may wish to open and view this file using your favorite ASCII editor (such as *Notepad* or *WordPad*).

5.4.2   Compiling the Source Code

Now the reaction module is ready for compilation. To create a dynamic link library (RXNS.DLL file), open a DOS window and go to the subdirectory where RXNS.F was saved and type the following command (this assumes that you have previously installed the *Digital FORTRAN* compiler):

```
fl32 /LD rxns_1.f
```

At this stage, the compiler will display all the syntax errors. If no changes have been made to the code, there shouldn't be any errors. If there are errors, fix them and recompile the code. After a successful compilation step, the compiler will create a DLL file (named as RXNS_1.DLL). Change the name of the DLL to RXNS.DLL

If you do not have access to a FORTRAN compiler but wish to continue with the tutorial, you can find a pre-compiled copy of rxns_1.dll in the tutorial\rt3d\userdef directory.

5.5   Testing and Debugging a New Reaction Package

After creating a new reaction package, it is always a good practice to test its response in a batch mode (i.e. how the reactions would behave in a batch reactor). For this purpose, we have developed a utility called BATCHRXN. This debugging tool can read the reaction information in a RXNS.DLL file and simulate its behavior in a batch mode.

To use BATCHRXN, it is recommended that the user define all the kinetic reaction parameters within the rxns subroutine (i.e. using method-#1). This is because the BATCHRXN code will not read information from RT3D input

files, including the RCT file. Therefore, a new reaction module should always be developed in a format similar to Method-#1 (or #2) and later, if required, the kinetic parameters can be moved into a RCT file to run RT3D simulations.

In addition to testing the new reaction module using BATHCHRXN, it is also a good practice to test the transport problem using RT3D in single-species tracer mode. Once a reaction package is tested using BATCHRXN, the DLL can be used with RT3D to run a full-fledged RT3D simulation.

5.5.1   Running BATCHRXN

Whenever BATCHRXN is executed, the code searches for a RXNS.DLL file in the local subdirectory. Thus, you should copy the RXNS.DLL file to the GMS directory (this is where the BATCHRXN.EXE and RT3D.EXE files are stored by default). While developing a new reaction module, always keep the source code (rxns*.f) in a local project directory, and rename and copy the DLL as RXNS.DLL into the GMS directory.

After you have copied the RXNS.DLL file into the GMS directory, open a *DOS* window and run the BATCHRXN code from your project subdirectory. The code will query for several input data. The queries and the appropriate responses for this example problem are given below:

```
Input-> ncomp, no_of_timesteps, delt
Format-> INTEGER, INTERGER, REAL
4 100 10.
Input-> Initial Values of y(i)
ncomp lines - One REAL entry per line
100.    *Initial PCE concentration in this case*
0.0     *Initial TCE concentration in this case*
0.0     *Initial DCE concentration in this case*
0.0     *Initial VC concentration in this case*
Do you want to change default atol & rtol: y/n
Default values are:- atol=1.0e-10 & rtol=1.0e-9
n
Input-> ncrxndata (number of reaction parameters)
Format-> INTEGER
0
```

You can also store these responses in a data file (say, batch.in) and use the command "batchrxn < batch.in" to automatically answer all the BATCHRXN queries. Here is an example batch.in file:

```
4 1000 1.
100.
0.
0.
0.
y
1.0e-11 1.0e-10
1.0e-11 1.0e-10
1.0e-11 1.0e-10
1.0e-11 1.0e-10
0
```

Note in the second case atol and rtol values are not initialized as default values, instead are set explicitly by the user.

5.5.2   **Viewing the Results**

After reading the input, BATCHRXN will execute and create an output file called batchrxn.out. The output file will contain a set of white-space separated ASCII data in column format (written using the Format statement 21E15.5). For our example problem, five columns are output: Time, specie-1 (PCE), specie-2 (TCE), specie-3 (DCE), and specie-4 (VC). Use any spreadsheet software such as *Excel* to plot and analyze this output data. The BATCHRXN output results for the example problem are shown in Figure 5.1.
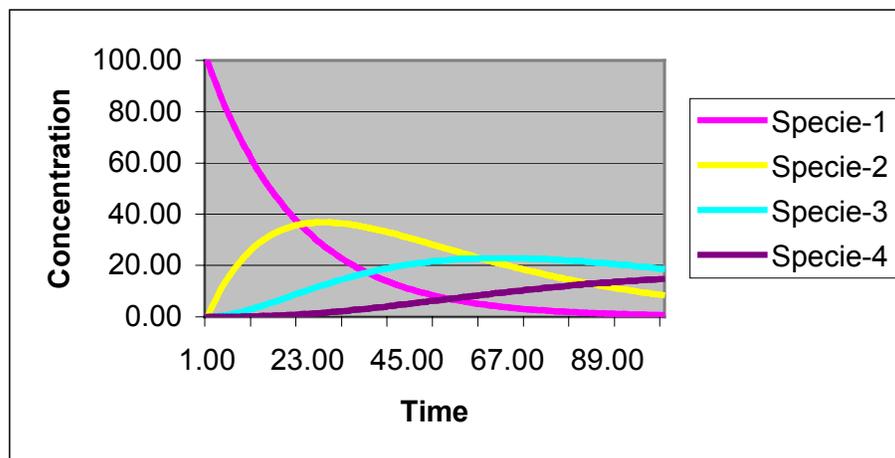
Figure 5.1   Sample Output from the BATCHRXN Code for the Sample Problem.

The results of a BATCHRXN run should be used to:

1. Debug errors in reaction expressions.

2. Check whether the reaction expressions and parameter values are reasonable (if available, microcosm or batch reactor data may be used to verify this).

3. Select appropriate values for numerical parameters atol (absolute tolerance) and rtol (relative tolerance).

The parameters atol and rtol are used by the differential equations solver to control convergence error while solving the reaction model. The differential equation solver will attempt to control a vector $e = e(i)$, which defines estimated local error (or convergence level) in a variable $y(i)$, according to the inequality: max-norm of $[e(i)/ewt(i)]$ is less than or equal to 1.0, where ewt =

(ewt(i)) is a vector of positive error weights and is computed using the formula: ewt(i) = rtol(i)*abs(y(i)) + atol(i).

We recommend the following rule of thumb to set atol and rtol values. If m is the number of significant digits required in the solution component y(i), set RTOL(i) = $10^{-(m+1)}$ and set ATOL(i) to a small value at which the absolute value of y(i) is essentially insignificant.

Note: since transport is not solved while executing batchrxn, all the retardation factors in the array reta() are automatically set to 1.0 with the DLL. However, if the same DLL is used with RT3D, appropriate species retardation factors will be transferred through the reta() array.

5.6   Setting up the RT3D Simulation

At this stage, we are ready to run a RT3D simulation using the newly developed reaction package. To do this, will define the transport model and enter the input data using the GMS interface. Once the model is built, we will save it to a set of RT3D input files and launch RT3D. When the user-defined reaction package option is selected, RT3D automatically launches the RXNS.DLL subroutine to solve the reaction terms.

5.7   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.

5.8   Required Modules/Interfaces

This tutorial utilizes the following components of the GMS interface:

- The *3D Grid* module

- The MODFLOW interface

- The RT3D interface

You can confirm whether each of these components has been enabled on your copy of GMS by selecting the *Register* command from the *File* menu. If you have licensed and enabled each of the listed items on your version of GMS, you can proceed to complete the tutorial in normal mode. If not, you will need to obtain an updated password or hardware lock before continuing.

5.9   Importing the MODFLOW Model

The first part of the simulation is to import the MODFLOW flow model. A steady state flow model has been previously computed and is supplied with the tutorial files.

1. Switch to the *3D Grid Module.*

2. Select the *Read Simulation* command in the *MODFLOW* menu.

3. In the *Open* dialog, locate and open the file entitled *tutorial\rt3d\flowmod\flowmod1.mfs.*

At this point, you should see a grid appear.

5.10   Building the Transport Model

Now that the flow model is established, the next step is to perform the RT3D simulation. For this part of the simulation, we will select the user-defined reaction option, define and initialize appropriate species and reaction parameters, and assign concentrations to the well.

5.10.1 Initializing the Model

To initialize the RT3D data:

Select the *New Simulation* command from the *MT3D* menu.

5.10.2 The BTN Package

The first step is to modify the data in the *Basic Transport Package*. First, we will select the user-defined reaction module option and name appropriate species and initialize their concentrations.

1. Select the *Basic Transport Package* command from the *MT3D* menu.

2. In the *Model* section, select the RT3D option.

3. Select the *Packages* button.

4. Select the *Advection Package*, the *Dispersion Package*, the *Source/Sink Mixing Package*, and the *Chemical Reaction Package*.

5. For the reaction type, select the *User-Defined Reaction* option.

6. Select the *OK* button to exit the *Packages* dialog.

Defining the Species

For a pre-defined reaction package, the appropriate list of species would be automatically loaded by GMS. However, for user-defined reactions, we must explicitly define the species.

1. Select the *Define species* button

2. If a name file appropriate to the user-defined reaction package is available, we can click on the *Import* button to initialize all species names in a single step (see Section 5.15). Since it is not available (we are using this new module for the first time), we have to define the species manually. To begin this process, click on the *New* button

3. Type the name of the species as: PCE

4. Leave the mobile option checked (this is the default)

5. Click on *New* again

6. Type the name of the species as: TCE

7. Click on *New* again

8. Type the name of the species as: DCE

9. Click on *New* again

10. Type the name of the species as: VC

11. Select the *OK* button.

Notice that the *Starting Concentration* section of the dialog now lists all the four species associated with our new reaction module. By default all of the starting concentrations are zero. Since the aquifer is assumed to be initially clean, we will simply accept the default values for starting concentrations.

Porosity

Next, we will define the porosity.

1. Select the *Porosity* button.

2. Select the *Constant -> Grid* button.

3. Enter a value of 0.3 and select *OK*.

4. Select the *OK* button to exit the *Porosity* dialog.

Setting up the Stress Periods

Next, we will define the stress periods. Since the injection rate and the boundary conditions do not change, we will use a single stress period with a length of 730 days (two years).

1. Select the *Stress Periods* button.

2. Select the *Initialize* button.

3. Enter 1 for the *No. of stress periods*, 730 for the *Length*, 10 for the *No. of time steps*, leave the *Transport step size* at 0.0, and select *OK*.

4. Select OK at the prompt.

5. Select the OK button to exit the *Stress Periods* dialog.

Output Options

Finally, we will define the output options. One binary solution file is created by RT3D for each of the species. By default, RT3D saves a solution at each transport step for each species. Since this results in large files containing more solutions than we need for the simple post-processing we intend to do, we will specify that a solution be saved every 73 days (every time step).

1. Select the *Output Control* button.

2. Select the Print at specified times option.

3. Select the *Times* button.

4. Select the *Initialize Values* button.

5. Enter 73.0 for the *Initial time step size*.

6. Enter 73.0 for the *Maximum time step size*.

7. Enter 730.0 for the *Maximum simulation time*.

8. Select the *OK* button to exit the *Initialize Time Steps* dialog.

9. Select the *Close* button to exit the *Variable Time Steps* dialog.

10. Select the *Close* button to exit the *Output Control* dialog.

This completes the input for the Basic Transport package.

> Select the *Close* button to exit the *Basic Transport Package* dialog.

5.10.3 The Advection Package

The next step is to initialize the data for the Advection package.

1. Select the *Advection Package* command from the *MT3D* menu.

2. Select the *Standard finite-difference method* option.

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

5.10.4 The Dispersion Package

Next, we will enter the data for the *Dispersion* package. The aquifer has a longitudinal dispersivity of 10.0 m and a transverse (horizontal) dispersivity of 3.0 m.

1. Select the *Dispersion Package* command in the *MT3D* menu.

2. Select the *Longitudinal Dispersivity* button.

3. Select the *Constant -> Grid* button.

4. Enter a value of 10.0 and select *OK*.

5. Select the *OK* button to exit the *Longitudinal Dispersivity* dialog.

6. Enter a value of 0.3 for the *Ratio of the trans. dispersivity to long. dispersivity* value.

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

5.10.5 The Source/Sink Mixing Package

Next, we will initialize the Source/Sink Mixing package and define the concentration at the spill location. We will define the concentrations at the wells by selecting the cells and assigning the concentration directly with the *Point Source/Sink* command. We will assign a concentration of 1000 mg/L for PCE and leave TCE, DCE, and VC concentrations at the default value of 0.0.

1. Select the *Select Cell* tool.

2. Select the well at the spill location.

3. Select the *Point Source/Sink* command in the *MT3D* menu.

4. Turn on the toggle in the *Well* section.

5. In the *Well* section, select the *PCE* species and enter a value of 1000.0 for concentration. Leave the other concentrations at zero.

6. Select the *OK* button to exit the *Point Source/Sink* dialog.

5.10.6   The Chemical Reaction Package

Next, we will review the data for the Chemical Reaction package.

Select the *Chemical Reaction Package* command in the *MT3D* menu.

Note that the reaction parameter box is blank. We will leave it blank in this case because in the DLL we coded all of the reaction constants directly within the reaction subroutine. We will demonstrate how to define them as user-defined variables later in this tutorial.

Select the *OK* button to accept the defaults.

5.11   Running RT3D

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

1. Select the *Save As* command from the *MT3D* menu.

2. In the *Save As* dialog, locate and open the directory entitled tutorial\rt3d\userdef.

3. Enter "rtmod1" for the file name.

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

To run RT3D:

1. Select the *Run RT3D* command from the *MT3D* menu.

2. Select *OK* at the prompt.

3. When the simulation is finished, close the window and return to GMS.

5.12   Viewing the Results

To view the results, select the *Read Solution* command from the *MT3D* menu and import the concentration files to view the results. To verify your results, compare the concentration values with the output from the tutorial entitled: *Sequential Anaerobic Degradation: PCE->TCE->DCE->VC*.

5.13   Developing a Reusable Reaction Package

Defining a new reaction model via a reaction package is a powerful option supported by the RT3D code. Once tested and developed, the reaction package (or DLL) can be used in other projects that have different conceptual flow and transport models. DLLs can also be distributed via web pages to other users who might be interested in modeling similar type of reactive transport systems. This section outlines the steps involved in developing a reusable version of reaction package.

In an earlier section, we mentioned that there are three different methods available for coding the reaction subroutine. Method-#1, which is the preferred method for testing and debugging a new reaction package, was discussed in detail in previous sections. Now, let's assume that we have sufficiently tested the reaction package and are ready to distribute the package to other users who might be interested in using it without having to recompile the code. To accomplish this, we have to re-code the reaction package based on either method-#2 or method-#3. We will utilize method-#3 (which is the most advanced method) here for demonstration purposes. As described earlier, method-#3 provides an option to let some or all of the reaction parameters be defined as spatially variable parameters. This method also allows the user to set the values of reaction parameters via the *.RCT input file (i.e., in the *Chemical Reactions Package* dialog in GMS).

5.13.1   Editing the Source Code

In this test problem, we have a total of seven reaction parameters. For illustration purposes, we will assume that five of them are constant parameters: K_{pce}, K_{tce}, Y_{tce_pce}, Y_{dce_tce}, and Y_{vc_dce} (note NCRXNDATA = 5), and two of them are spatially variable parameters: K_{dce} and K_{vc} (note NVRXNDATA = 2). The following FORTRAN listing for the reaction module (using method-#3) incorporates these changes:

```
        SUBROUTINE rxns(ncomp,nvrxndata,j,i,k,y,dydt,
     $           poros,rhob,reta,rc,nlay,nrow,ncol,vrc)
c ***** Block 1: Comments block *******
c2345678901234567890123456789012345678901234567890123456789012
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 [array variable dpreta(mcomp)]
c rhob -  Bulk density of the node
c rc - Stores spatially constant reaction parameters (up to 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: 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 First_time
      DATA First_time/1/
      DOUBLE PRECISION y,dydt,poros,rhob,reta
      DOUBLE PRECISION rc,vrc
```

```
          DIMENSION y(ncomp),dydt(ncomp),rc(50)
          DIMENSION vrc(ncol,nrow,nlay,nvrxndata),reta(50)
C ****** End of block 2 *******

C *** Block 3: Declare your problem-specific new variables here ***
C     INTEGER
      DOUBLE PRECISION pce,tce,dce,vc,kpce,ktce,kdce,kvc
      DOUBLE PRECISION ytcepce,ydcetce,yvcdce
C ***** End of Block 3   ******

C *** Block 4: INITIALIZE YOUR CONSTANTS HERE, IF DESIRED ***
      IF (First_time .EQ. 1) THEN
         kpce = rc(1)  !PCE first-order degradation rate (constant)
         ktce = rc(2)  !TCE first-order degradation rate (constant)
c        kdce is a spatially variable parameter, it is defined in block-5
c        kvc is a spatially variable parameter, it is defined in block-5
         ytcepce = rc(3)
         ydcetce = rc(4)
         yvcdce = rc(5)
         First_time = 0 !reset First_time to skip this block later
      END IF
C ***** End of Block 4   ******

C  *** Block 5: Definition of other variable names ***
      pce = y(1)
      tce = y(2)
      dce = y(3)
      vc = y(4)
      kdce = vrc(j,i,k,1)!Spatially variable DCE decay rate
      kvc = vrc(j,i,k,2)  ! Spatially variable vc decay rate
C ***** End of Block 5   ******

c  ***  Block 6: Definition of Differential Equations ***
      dydt(1) = -kpce*pce/reta(1)
      dydt(2) = (-ktce*tce + kpce*pce*ytcepce)/reta(2)
      dydt(3) = (-kdce*dce + ktce*tce*ydcetce)/reta(3)
      dydt(4) = (-kvc*vc + kdce*dce*yvcdce)/reta(4)
C ***** End of Block 6   ******

      RETURN
      END
```

Note that this subroutine is identical to the previous version except that in blocks 4 and 5, the rc() and vrc() arrays are used to initialize reaction parameters. The values of the parameters will be defined in the RT3D input file *.RCT. In the section below, we will demonstrate how the reaction parameter values can be defined efficiently using the GMS interface.

5.13.2   Compiling the Source Code

Now follow the steps detailed in Section 5.4 to compile and create a new rxns.dll file. The FORTRAN source code is provided in the following file:

```
tutorial\rt3d\userdef\rxns_2.f
```

Once the source is compiled, rename the DLL as rxns.dll and copy it to the GMS subdirectory where RT3D.EXE is saved. If you wish to preserve the previous version of the rxns.dll file, you will need to rename the old version before copying the new version to the GMS directory.

Once again, if you do not have access to a FORTRAN compiler but wish to continue with the tutorial, you can find a pre-compiled copy of rxns_2.dll in the tutorial\rt3d\userdef directory.

5.14   Modifying the Transport Model

We are now ready to use the new module for reactive transport simulations. If you have exited GMS, or if you have made any changes to the RT3D simulation defined above, you will need to re-import both the MODFLOW and RT3D simulation.

5.14.1   The Chemical Reaction Package

Next, we will define and initialize the chemical reaction parameters.

Select the *Chemical Reaction Package* command in the *MT3D* menu.

Note that the reaction parameter box is blank. In this section, we will define and initialize the reaction parameters.

1. Click on *Define Parameters* button.

2. Once again, if a name file appropriate to the user-defined reaction package, is available, we can click on the *Import* button and initialize all reaction parameter names in a single step (see Section 5.15). Since it is not available in this case, we will define them manually. To begin this process, click on *New* button.

3. Enter the name of reaction parameter as: Kpce.

4. Do NOT select the *Spatially variable* option (it is off by default).

5. Click on *New*.

6. Enter the name of reaction parameter as: Ktce

7. Click on *New*.

8. Enter the name of reaction parameter as: Kdce

9. Turn on the *Spatially variable* option.

10. Click on *New*.

11. Enter the name of reaction parameter as: Kvc

12. Turn on the *Spatially variable* option.

13. Click on *New*.

14. Enter the name of reaction parameter as: Ytce_pce

15. Click on *New*.

16. Enter the name of reaction parameter as: Ydce_tce

17. Click on *New*.

18. Enter the name of reaction parameter as: Yvc_dce

19. Select the *OK* button.

Now notice in the *Define Parameters* section all the reaction parameters are listed. Next, we will assign values for all these parameters.

1. In the *Reaction Parameters* section, click on K_{pce} and set the constant value to 0.005.

2. Click on K_{tce} and set the constant value to 0.003

3. Click on Y_{tce_pce} and set the constant value to 0.792

4. Click on Y_{dce_tce} and set the constant value to 0.738

5. Click on Y_{vc_dce} and set the constant value to 0.644

6. Now, click on K_{dce}(variable).

7. Select the *Edit* button next to the *Parameter Value* edit field.

8. Click the *Constant to Grid* button.

9. Enter a value of 0.002 and select *OK*.

10. Click on K_{vc} (variable).

11. Select the *Edit* button next to the *Parameter Value* edit field.

12. Select the *Constant to Grid* button.

13. Enter a value of 0.001 and select *OK*.

14. Select the *OK* button to exit the *RT3D Chemical Reaction Package* dialog.

We have defined five spatially constant reaction parameters and two spatially variable reaction parameters. Therefore, in the *.RCT package file, NCRXNDATA will be set to 5 and NVRXNDATA will be set to 2. During execution, the RT3D code stores and transfers all the constant reaction parameters through a one-dimensional reaction constant array rc(). The parameter values are transferred in the order in which they are originally entered; i.e. K_{pce} is stored in rc(1), K_{tce} is stored in rc(2) and so on. Similarly, all the variable reaction parameters are stored and transferred through a four-dimensional variable reaction constant array vrc().

Note that although two of the reaction parameters can vary spatially, for the sake of keeping this tutorial simple, we have assigned a single value to all cells in both cases. The reaction parameters can be edited on a cell by cell basis using the *Array Editor* dialog in the *Chemical Reaction Package* dialog or by selecting a set of cells and selecting the *Cell Attributes* command in the *MT3D* menu.

5.14.2   Running RT3D

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

1. Select the *Save As* command from the *MT3D* menu.

2. Check to ensure that the directory is still set to *tutorial\rt3d\userdef*.

3. Enter "rtmod2" for the file name.

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

To run RT3D:

1. Select the *Run RT3D* command from the *MT3D* menu.

2. Select *OK* at the prompt.

3. When the simulation is finished, close the window and return to GMS.

5.14.3   Viewing the Results

Select the *Read Solution* command from the *MT3D* menu and import the appropriate concentration files to view the results. The results should be similar to those computed earlier.

5.15   Creating a Name File for GMS import

When a new reaction package is created, the package developer should create a name file. The information regarding species names, species types, species order, reaction parameter names, reaction parameter types, and reaction parameter sequence are stored in a name file. All of the information needed for a name file is included in the RT3D super file created by GMS. Thus, the simplest way to create the name file is to set up the first simulation using the steps defined above and then open the RT3D super file for the simulation (*.rts) in a text editor. Delete all the cards except the first card, and the cards beginning with SPC and RXNPARAM. The edited file should look like this:

```
RT3DSUP
SPC "PCE" 1 1
SPC "TCE" 2 1
```

```
SPC "DCE" 3 1
SPC "VC" 4 1
RXNPARAM "kdce" 3 1
RXNPARAM "kvc" 4 1
RXNPARAM "kpce" 1 0
RXNPARAM "ktce" 2 0
RXNPARAM "Ytce_pce" 5 0
RXNPARAM "Ydc_tce" 6 0
RXNPARAM "Yvc_dce" 7 0
```

Save this information in a new file, say "specie.nam". This file can be later used for directly importing species and reaction parameter information. Whenever a user-defined reaction package (as a DLL or source code) is distributed to an another GMS user, a specie name file, appropriate to the reaction package, should be included with it.

5.15.1 Importing Species Names

The specie name file can be used to set-up a new RT3D transport problem using a (previously developed) user-defined reaction package. To import the specie names into GMS, select *Basic Transport Package*, click on the *Define Species* option, click on the *Import* button, and read the "specie.nam" file. These steps will import appropriate specie names in the correct order.

5.15.2 Importing Reaction Parameter Names

To import reaction parameter names, select *Chemical Reaction Package*, click on *Define Parameters* option, click on *Import* button, and read the "specie.nam" file again. This will import appropriate reaction parameter names in the correct order.

5.16   Special Instructions for UNIX Users

Since development of a DLL requires *Microsoft* or *Digital's visual FORTRAN* compiler specific commands, this option is incompatible with *Unix* platforms. Therefore, *Unix* users should always comment the first line in the block-2 of rxns.f file that begin with a command "!MS$ATTRIBUTES". Also whenever any changes are made to the RXNS.F code, the RT3D executable should to be recreated, using a FORTRAN-90 compiler, by linking RXNS.OBJ with the RT3D.LIB (to use RT3D) or with BATCHRXN.LIB (to use BATCHRXN).

5.17   Conclusion

This concludes the *User-Defined Reactions* tutorial. If you wish to exit GMS at this time:

1.   Select the *Exit* command from the *File* menu.

2. Select the *No* button at the prompt.

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.

6.1 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:

$$\frac{\partial C}{\partial t} + \frac{\rho}{\phi}\frac{\partial \widetilde{C}}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right) - \frac{\partial}{\partial x_i}(v_i C) + \frac{q_s}{\phi}C_s \dots\dots\dots\dots\dots\dots\dots\dots(6.1)$$

$$\frac{\rho}{\phi}\frac{\partial \widetilde{C}}{\partial t} = \xi\left(C - \frac{\widetilde{C}}{\lambda}\right) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(6.2)$$

where C is the concentration of the contaminant in the mobile-phase [ML^{-3}], $\widetilde{C}$ is the concentration of the contaminant in the immobile phase (mass of the contaminants per unit mass of porous media, [MM^{-1}]), ρ 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^{3}M^{-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:

$$\frac{dC}{dt} = -\xi\left(C - \frac{\widetilde{C}}{\lambda}\right) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(6.3)$$

$$\frac{d\widetilde{C}}{dt} = \frac{\phi\xi}{\rho}\left(C - \frac{\widetilde{C}}{\lambda}\right)$$ .... (6.4)

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

6.2   Description of Problem

The example problem we will be solving in this tutorial is shown in Figure 6.1. The site is a 1000 ft x 500 ft 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 4000 ft^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 1.0×10^{-7} (L/mg), soil dry bulk density, ρ, is assumed to be 1.5×10^6 (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, $\widetilde{C} = \lambda C$, can be estimated to be at 3×10^{-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 $\xi = 0.1$ day^{-1}), intermediate conditions (using $\xi = 0.002$ 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.
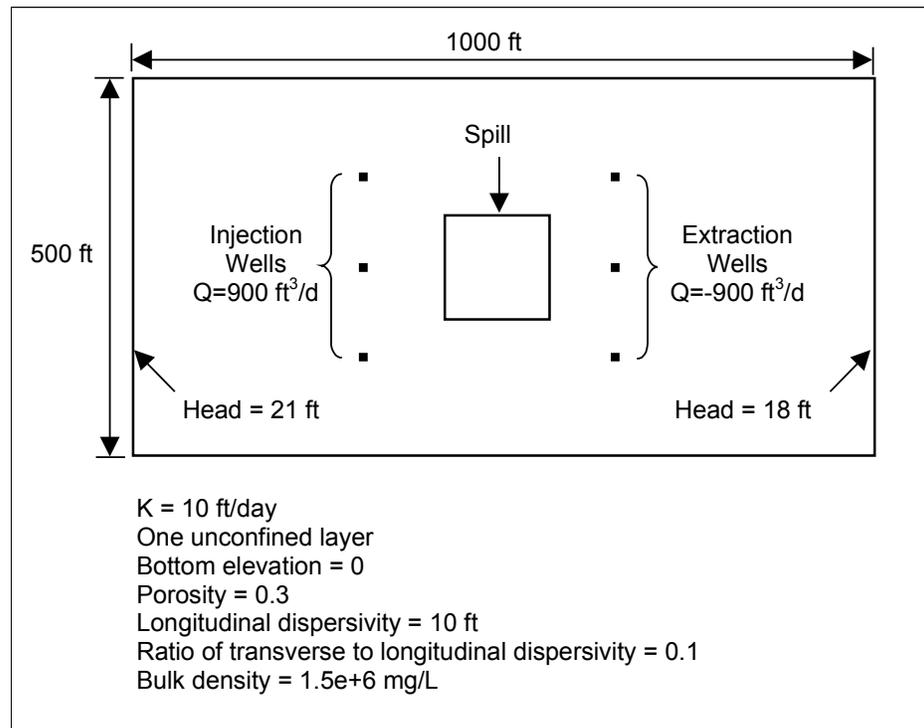
Figure 6.1   Sample Problem.

6.3   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.

6.4   Required Modules/Interfaces

This tutorial utilizes the following components of the GMS interface:

- The *Map* module

- The *3D Grid* module

- The MODFLOW interface

- The RT3D interface

You can confirm whether each of these components has been enabled on your copy of GMS by selecting the *Register* command from the *File* menu. If you have licensed and enabled each of the listed items on your version of GMS,

you can proceed with the tutorial in normal mode. If not, you will need to obtain an updated password or hardware lock before continuing.

6.5   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 20 ft X 20 ft cells. The flow solution will then be used to drive the transport model.

6.5.1   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 *Open* command in the *File* menu.

2. Change the file filter to *Map Files (*.map)*.

3. In the *Open* dialog, locate and open the file entitled *tutorial\rt3d\rlimsorp\site.map*

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

6.5.2   Creating the Grid

To create the grid:

1. Switch to the *3D Grid* module

2. Select the *Create Grid* command from the *Grid* menu.

3. In the *X-Dimension* section, set the *Length* to 1000 and the *Number of cells* to 50.

4. In the *Y-Dimension* section, set the *Length* to 500 and the *Number of cells* to 25.

5. In the *Z-Dimension* section, set the *Number of cells* to 1.

6. Select the *OK* button.

6.5.3   Initializing the MODFLOW Data

To initialize the MODFLOW data:

Select the *New Simulation* command in the *MODFLOW* menu.

6.5.4   The Basic Package

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

1. Select the *Basic Package* command from the *MODFLOW* menu.

2. For the first heading, enter "Flow Model".

3. For the second heading, enter your name.

Units

To define the units:

1. Select the *Units* button.

2. For the *Length* units, select *ft*.

3. For the *Time* units, select *d*.

4. For the *Mass* units, select *mg*.

5. For the *Concentration* units, select *mg/l*.

Note that these same units will be used for the RT3D simulation. We can ignore the *Force* unit.

Packages

Next, we will select the packages.

1. Select the *Packages* button.

2. Turn on the *Well* package.

3. 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 21 ft everywhere in the grid.

1. Select the *Starting Heads* button.

2. Select the *Constant -> Layer* button.

3. Enter a value of 21.

4. Select the *OK* button twice to return to the *Basic Package* dialog.

5. Select the *Close* button to exit the *Basic Package* dialog.

Specified Head Boundaries

Next, we will define the specified head boundaries.

6. Choose the *Select J tool*

7. Click once in any of the cells in the leftmost column of the grid.

8. Select the *Cell Attributes* command in the *MODFLOW* menu.

9. Change the *IBOUND* value to −1 and leave the *Starting head* value unchanged at 21.0.

10. Select the *OK* button.

11. Click once in any of the cells in the rightmost column of the grid.

12. Select the *Cell Attributes* command in the *MODFLOW* menu.

13. Change the *IBOUND* value to −1.

14. Change the *Starting head* value to 18.

15. Select the *OK* button.

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

This concludes the input for the Basic package.

6.5.5   The BCF Package

Next, we will define the input for the BCF package.

Select the *BCF Package* command from the *MODFLOW* menu.

Hydraulic Conductivity

The hydraulic conductivity is constant throughout the grid.

1. Select the *Horizontal Hyd. Conductivity* button.

2. Select the *Constant -> Layer* button.

3. Enter a value of 10.

4. Select the *OK* button twice to return to the *BCF Package* dialog.

Top Elevation

The top elevation is a constant value of 25 m throughout the grid.

1. Select the *Top Elevation* button.

2. Select the *Constant -> Layer* button.

3. Enter a value of 25.

4. Select the *OK* button twice to return to the *BCF 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.

5. Select the *Close* button to exit the *BCF Package* dialog.

6.5.6   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 *Edit Window*, 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 *Point Sources/Sinks* command from the *MODFLOW* menu.

5. In the *Well* section, select the *Add* button.

6. Enter a value of 900 for *Flow*.

7. Select the *OK* button.

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

To create the extraction wells:

1. While holding down the *Shift* key, locate and select the cells at (I=7, J=33), (I=13, J=33) and (I=19, J=33).

2. Select the *Point Sources/Sinks* command from the *MODFLOW* menu.

3. In the *Well* section, select the *Add* button.

4. Enter a value of -900 for *Flow*.

5. Select the *OK* button.

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

6.5.7   Saving and Running the Flow Model

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

1. Select the *Save As* command from the *MODFLOW* menu.

2. Make sure the path is still set to *tutorial\rt3d\rlimsorp*.

3. Enter "flowmod" for the file name.

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

To run MODFLOW:

1. Select the *Run* MODFLOW command from the *MODFLOW* menu.

2. Select *OK* at the prompt.

3. When the simulation is finished, close the MODFLOW window and return to GMS.

6.5.8   Viewing the Solution

Finally, before proceeding to build the transport model, we will import and view the flow solution.

1. Select the *Read Solution* command from the *MODFLOW* menu.

2. Select *OK* at the prompt.

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.

6.6   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.

6.6.1   Initializing the Model

To initialize the RT3D model:

> Select the *New Simulation* command in the *MT3D* menu.

6.6.2   The Basic Transport Package

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

1. Select the *Basic Transport Package* command from the *MT3D* menu.

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

3. For the first heading, enter "Transport Model – Retardation Condition".

4. Enter your name for the second heading.

Packages

Next, we will select which packages we will use:

1. Select the *Packages* button.

2. Turn on all four packages.

3. In the RT3D *Reactions* section, select the reaction titled *Rate-Limited Sorption Reactions*.

4. Select the *OK* button.

Stress Periods

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

1. Select the *Stress Periods* button.

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. We will change this so that a solution is output every 200 days.

1. Select the *Output Control* button.

2. Select the *Print at specified times* option.

3. Select the *Times* button.

4. Select the *Initialize Values* button.

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 *Close* button to exit the *Variable Time Steps* dialog.

10. Select the *Close* button to exit the *Output Control* dialog.

Porosity

To enter the porosity:

1. Select the *Porosity* button.

2. Select the *Constant -> Layer* button.

3. Enter a value of 0.3.

4. Select the *OK* button twice to return to the *Basic Transport Package* dialog.

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.

1. Select the *Close* button to exit the *Basic Transport Package* dialog.

2. 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.

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

2. Select the *Cell Attributes* command in the *MT3D* menu.

3. Make sure that *Aqueous conc.* is highlighted and enter a value of 300 for the starting concentration.

4. Highlight the *Solid conc.* item and enter a value of 3.0e-5 for the starting concentration.

5. Select the *OK* button.

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

This completes the input for the Basic Transport package.

6.6.3   The Advection Package

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

1. Select the *Advection Package* command from the *MT3D* menu.

2. Select the *Modified method of characteristics* option.

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* dilaog.

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

6.6.4   The Dispersion Package

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

1. Select the *Dispersion Package* command from the *MT3D* menu.

2. Select the *Longitudinal Dispersivity* button.

3. Select the *Constant -> Layer* button.

4. Enter a value of 10.

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

6. Enter a value of 0.1 for the *Ratio of trans. dispersivity to long. dispersivity* value.

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

6.6.5   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. From the *MT3D* menu, select the *Point Sources/Sinks* command.

3. Turn on the *Well* option.

4. Leave the concentration at zero and select the *OK* button to exit.

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

6.6.6   The Reaction Package

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

1. Select the *Chemical Reaction Package* command from the *MT3D* menu.

2. Enter a value of 1.5e6 for the *Bulk Density*.

3. In the *Reaction Parameters* section, make sure that the *mass transfer coeff.* item is highlighted and enter a constant value of 0.1.

4. Highlight the *partitioning coeff.* item and enter a value of 1.0e-7.

5. Select the *OK* button to exit.

6.6.7   Saving and Running the Simulation

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

1.   Select the *Save As* command from the *MT3D* menu.

2.   Enter "retard" for the file name.

3.   Select the *Save* button to exit the *Save File* dialog.

To run RT3D:

1.   Select the *Run RT3D* command from the *MT3D* menu.

2.   Select *OK* at the prompt.

3.   When the simulation is finished, close the RT3D window and return to GMS.

6.6.8   Viewing the Solution

To view the RT3D solution:

1.   Select the *Read Solution* command from the *MT3D* menu.

2.   Select the OK button at the prompt.

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

Select the *600* time step from the TS combo box at the top of the GMS window.

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

1.   Select the *Contour Options* command from the *Data* menu.

2.   In the lower right corner of the dialog, select the *Use color ramp* option.

3.   Select the *Color Ramp Options* button.

4.   Select the *Show color legend* option.

5.   Select the *OK* button to exit the *Color Ramp Options* dialog.

6.   Select the *OK* button to exit the *Contour Options* dialog.

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

Select the *Aqueous conc* item from the *Data Set* combo box at the top of the GMS window.

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

6.7   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.

6.7.1   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 *Read Solution* command from the *MT3D* menu.

2. Click on the *Select Simulation* button.

3. Select the file entitled *othersol.rts*.

4. 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.

6.7.2   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:

Using the *TS* combo box, 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.

6.7.3   Comparing the Solid Phase Concentrations

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

1. Using the *Solution* combo box, select the *Retard (RT3D)* solution.

2. Using the *Data Set* combo box, 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.

1. Using the *Solution* combo box, select the *othersol (RT3D)* solution.

2. Using the *Data Set* combo box, 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.

Using the *Data Set* combo box, select the *Solid (sequest)*data set.

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

6.8   Conclusion

This concludes the tutorial: *Rate-Limited Sorption Reaction*. If you wish to exit GMS at this time:

1. Select the *Exit* command from the *File* menu.

2. Select the *No* button at the prompt.

CHAPTER 7

Double Monod Model

This tutorial illustrates the steps involved in using GMS and RT3D to model the reaction between an electron donor and an electron acceptor, mediated by an actively growing microbial population that exist in both soil and aqueous phases. Since the flow model used in this simulation is similar to the flow model used in *Chapter 2 - Instantaneous Aerobic Degradation*, the steps involved in building the flow model will not be described in this tutorial. A pre-defined version of the flow model will be used.

7.1   Description of the Reaction Model

Methods for enhancing in situ bioremediation of subsurface soil and groundwater involve injection or infiltration of a carbon source (or electron donor), nutrients, and other electron acceptors to stimulate the growth of native microbes. In addition, bioengineered suspension cultures of contaminant degrading organisms may be also added to increase the amount of attached and suspended biomass in the subsurface. These two types of active remediation techniques can be used to bioremediate contaminated source zones or to establish a biobarrier to prevent plume migration and/or to enhance plume attenuation. The successful use of subsurface microbes for bioremediation requires an understanding of coupled flow, transport, and reaction processes that control bacterial growth and migration patterns. The Dual-Monod model, available in the RT3D code, can be used to develop such understanding by simulating the coupled reactive transport and microbial growth. The model is developed in a general format; therefore, the interaction between any electron donor and acceptor mediated by any type of microbial population can be simulated by varying appropriate kinetic constants. Advanced users can modify this basic formulation and couple it with other packages, such as the

sorption package, to simulate more realistic bioremediation scenarios (any such modified reaction models can be easily implemented via the user-defined reaction option).

Assuming the linear-equilibrium model for modeling sorption, and the Dual-Monod model for modeling bacterial growth, the fate and transport equation for an electron donor (hydrocarbon, for example) in a multi-dimensional saturated porous media can be written as:

$$R_D \frac{\partial [D]}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial [D]}{\partial x_j}\right) - \frac{\partial}{\partial x_i}\left(v_i[D]\right) + \frac{q_s}{\phi}[D_s] -$$
$$\mu_m\left([X] + \frac{\rho \widetilde{X}}{\phi}\right)\left(\frac{[D]}{K_D + [D]}\right)\left(\frac{[A]}{K_A + [A]}\right) \quad\text{................................(7.1)}$$

where [D] is the electron donor concentration in the aqueous phase [ML^{-3}], [D$_s$] is the donor concentration in the sources/sinks [ML^{-3}], D_{ij} is the dispersion coefficient; [X] is the aqueous phase bacterial cell concentration [ML^{-3}], $\widetilde{X}$ is the solid-phase cell concentration (mass of bacterial cells per unit mass of porous media [MM^{-1}]), [A] is the electron acceptor concentration in the aqueous phase [ML^{-3}], R$_H$ is the retardation coefficient of the hydrocarbon, K$_D$ is the half saturation coefficient for the electron donor [ML^{-3}], K$_A$ is the half saturation coefficient for the electron acceptor [ML^{-3}], and μ_m is the contaminant utilization rate [T^{-1}]. The model assumes that the degradation reactions occur only in the aqueous phase, which is usually a conservative assumption.

The fate and transport of the electron donor (oxygen, for example) can be modeled using the equation:

$$R_A \frac{\partial [A]}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial [A]}{\partial x_j}\right) - \frac{\partial}{\partial x_i}\left(v_i[A]\right) + \frac{q_s}{\phi}[A_s] -$$
$$Y_{A/D}\,\mu_m\left([X] + \frac{\rho \widetilde{X}}{\phi}\right)\left(\frac{[D]}{K_D + [D]}\right)\left(\frac{[A]}{K_A + [A]}\right) \quad\text{..........................(7.2)}$$

where Y$_{A/D}$ is the stoichiometric yield coefficient, and R$_A$ is the retardation coefficient of the electron acceptor.

The fate and transport of bacteria in the aqueous phase can be described using the equation:

$$\frac{\partial[X]}{\partial t} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial[X]}{\partial t}\right) - \frac{\partial}{\partial x_i}\left(v_i[X]\right) + \frac{q_s}{\phi}[X_s] - K_{att}[X] + \frac{K_{det}\rho\widetilde{X}}{\phi} +$$

$$Y_{X/D}\mu_m[X]\left(\frac{[D]}{K_D+[D]}\right)\left(\frac{[A]}{K_A+[A]}\right) - K_e[X] \quad\quad \dots\dots\dots\dots (7.3)$$

where K_{att} is the bacterial attachment coefficient $[T^{-1}]$, K_{det} is the bacterial detachment coefficient $[T^{-1}]$, and K_e is the endogenous cell death or decay coefficient $[T^{-1}]$.

The growth of attached-phase bacteria can be described using an ordinary differential equation of the form:

$$\frac{d\widetilde{X}}{dt} = \frac{K_{att}\phi[X]}{\rho} - K_{det}\widetilde{X} + Y_{X/D}\mu_m\widetilde{X}\left(\frac{[D]}{K_D+[D]}\right)\left(\frac{[A]}{K_A+[A]}\right)$$

$$- K_e\widetilde{X} \quad\quad \dots\dots\dots (7.4)$$

The conceptual model used here for representing attached bacteria cells is similar to the macroscopic model described by Baveye and Valocchi (*Wat. Resour. Res.,* 25, 1413-1421,1989). The model also assumes first-order kinetic expressions for representing bacterial attachment and detachment processes (Taylor and Jaffe, *Wat. Resour. Res.,* 26, 2181-2194,1990, and Hornberger et al., *Wat. Resour. Res.,* 28, 915-938, 1992). Permeability and porosity changes caused by bacterial growth are ignored in this formulation. However, if required, macroscopic models for biomass-affected porous-media properties described by Clement et al. (*Ground Water*, 34, 934-942, 1996) may be integrated within this modeling approach. It should be noted that a lot of active research is currently underway to gain an increased understanding of bacteria transport in porous media because currently available bacterial transport models (including the model used here) are arguably approximate. Therefore, application of this model to real situations should be always supported by field- or laboratory-scale data.

The reactive-transport model discussed above was set-up as a RT3D reaction package with three mobile species (to represent electron donor, electron acceptor, and aqueous bacteria) and one immobile species (to represent attached soil bacteria). After employing the reaction-operator splitting strategy, the reaction package for the problem reduces to:

$$\frac{d[D]}{dt} = -\frac{\mu_m}{R_D}\left([X] + \frac{\rho\widetilde{X}}{\phi}\right)\left(\frac{[D]}{K_D+[D]}\right)\left(\frac{[A]}{K_{[A]}+[A]}\right) \quad\quad \dots\dots\dots\dots (7.5)$$

$$\frac{d[A]}{dt} = -\frac{Y_{A/D}\mu_m}{R_A}\left([X] + \frac{\rho\widetilde{X}}{\phi}\right)\left(\frac{[D]}{K_D+[D]}\right)\left(\frac{[A]}{K_A+[A]}\right) \quad\quad \dots\dots\dots\dots (7.6)$$

$$\frac{d[X]}{dt} = -Y_{X/D}\,\mu_m\left([X]+\frac{\rho\widetilde{X}}{\phi}\right)\left(\frac{[D]}{K_D+[D]}\right)\left(\frac{[A]}{K_A+[A]}\right)+$$

$$\frac{K_{det}\rho\widetilde{X}}{\phi}-K_{att}[X]-K_e[X]$$

.......................(7.7)

$$\frac{d\widetilde{X}}{dt} = \frac{K_{att}\,\phi[X]}{\rho} - K_{det}\,\widetilde{X} + Y_{X/D}\,\mu_m\,\widetilde{X}\left(\frac{[D]}{K_D+[D]}\right)\left(\frac{[A]}{K_A+[A]}\right) - K_e\widetilde{X}$$

(7.8)

These four equations are coded into the double-monod reaction module.

7.2   Description of Problem

The problem we will be solving in this tutorial is similar to the problem described in the first tutorial (Figure 2.1). The site is a 510 m X 310 m section of a confined aquifer with a flow gradient from left to right. An underground storage tank is leaking fuel hydrocarbon contaminants at 2 m³/day at the location shown. Source concentration of BTEX is 500 mg/L. It will be assumed that the aquifer is initially clean and has very low levels of aerobic bacterial activity. The fuel hydrocarbon compounds are expected to serve as the carbon source, resuscitating the bacterial cells and activating them into a growth mode. This is a common subsurface phenomenon that occurs in most fuel-contaminated sites. Several field studies have observed the presence of enhanced levels of microbial activity near a source region, and low background levels outside the plume. In this example, we will simulate the transient changes in hydrocarbon, oxygen, and bacterial concentrations levels within the contaminated area.

Initial levels of hydrocarbon, oxygen, aqueous bacteria, and attached bacteria are assume to be: 0.0 mg/L, 9.0 mg/L, 2 x 10^{-17} (value for X in mg/L), and 3.0 x 10^{-9} (value for $\widetilde{X}$ in mg of bacteria/mg of soil), respectively. Note the mass fraction unit used for representing soil bacterial cells will always yield small numbers. Using the value of soil porosity and bulk density, these numbers can be converted into standard mg/L units (liquid-volume basis) to get a better feel for bacterial concentration levels. For example, assuming $\rho = 1.6$ x 10^6 mg/L and $\phi = 0.3$, the initial value of soil bacterial concentration can be expressed (converted to liquid volume basis using the formula: $\widetilde{X}\rho/\phi$) as: 0.016 mg/L. While post processing output concentration in GMS, the data calculator will be used to perform this unit conversion. This is recommended because extremely small numbers may not be displayed correctly in GMS.

Assumed values for other kinetic reaction constants are given below:

Constant	GMS Display	Value
μ_m	umax	0.125 day^{-1}
K_D	K_{ed}	0.12 mg/L
K_A	K_{ea}	0.1 mg/L
$Y_{x/D}$	$Y_{x/ed}$	0.05
$Y_{A/D}$	$Y_{ea/ed}$	3.0
K_{decay}	K_{decay}	0.001 day^{-1}
K_{att}	K_{att}	70.0 day^{-1}
K_{det}	K_{det}	1.0 day^{-1}

Sorption is assumed to be negligible for this site, hence the value of all retardation coefficients are assumed to be unity.

The first part of the problem will be to import a previously computed MODFLOW flow model of the site. Using this flow field, a reactive transport model will be then be defined using RT3D.

7.3   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.

7.4   Required Modules/Interfaces

This tutorial utilizes the following components of the GMS interface:

- The *3D Grid* module

- The MODFLOW interface

- The RT3D interface

You can confirm whether each of these components has been enabled on your copy of GMS by selecting the *Register* command from the *File* menu. If you have licensed and enabled each of the listed items on your version of GMS, you can proceed to complete the tutorial in normal mode. If not, you will need to obtain an updated password or hardware lock before continuing.

7.5   Importing the MODFLOW Model

The first part of the simulation is to import the MODFLOW flow model. A steady state flow model has been previously computed and is supplied with the tutorial files.

1. Switch to the *3D Grid Module*

2.   Select the *Read Simulation* command in the *MODFLOW* menu.

3.   In the *Open* dialog, locate and open the file entitled *tutorial\rt3d\flowmod\flowmod1.mfs*.

At this point, you should see a grid appear.

7.6   Building the Transport Model

Now that the flow model is imported, the next step is to perform the RT3D simulation. For this part of the simulation, we will select the reaction, define the reaction data, define the supplemental layer data needed by RT3D, define the boundary conditions, and assign concentrations to the well.

7.7   Initializing the Model

To initialize the RT3D data:

Select the *New Simulation* command from the *MT3D* menu.

7.8   The BTN Package

The next step is to initialize the data in the Basic Transport Package. First, we will initialize the data, select RT3D as the transport model, and select the appropriate packages.

1.   Select the *Basic Transport Package* command from the *MT3D* menu.

2.   Select the *RT3D* option.

3.   Select the *Packages* button.

4.   Select the *Advection Package*, the *Dispersion Package*, the *Source/Sink Mixing Package*, and the *Chemical Reaction Package*.

5.   For the reaction type, select the *Double Monod Model* option.

6.   Select the *OK* button to exit the *Packages* dialog.

7.8.1   Starting Concentration

Note that in the *Starting Concentration* section of the dialog, the species associated with the reaction we are modeling are listed by name. The next step is to define the starting concentration for each of these species. The default

starting concentration is zero. We will use the default value for the electron donor, but we will use non-zero values for the electron acceptor (9.0 mg/L), the aqueous phase bacteria ($2x10^{-17}$ mg/L), and the solid phase bacteria ($3x10^{-9}$ mg bacteria/mg of soil).

1. Select *Electron Acceptor* from the list of species.

2. Select the *Starting Concentration* button.

3. Select the *Constant -> Grid* button.

4. Enter a value of 9.0.

5. Select the *OK* button.

6. Select the *OK* button to exit the *Starting Concentration* dialog.

7. Repeat these steps to enter a starting value of 2e-17 for the *Aqueous-Phase Bacteria* and 3e-9 for the *Solid-Phase Bacteria*.

7.8.2   Porosity

Next, we will define the porosity.

1. Select the *Porosity* button.

2. Select the *Constant -> Grid* button.

3. Enter a value of 0.3 and select *OK*.

4. Select the *OK* button to exit the *Porosity* dialog.

7.8.3   Stress Periods

Next, we will define the stress periods. Since the injection rate and the boundary conditions do not change, we will use a single stress period with a length of 730 days (two years).

1. Select the *Stress Periods* button.

2. Enter a value of 730 for the *Length*.

3. Enter a value of 10 for the *No. of time steps*.

4. Select the *OK* button to exit the *Stress Periods* dialog.

7.8.4   Output Options

Finally, we will define the output options. One binary solution file is created by RT3D for each of the species. By default, RT3D saves a solution at each transport step for each species. Since this results in large files containing more solutions than we need for the simple post-processing we intend to do, we will specify that a solution be saved every 73 days (every time step).

1. Select the *Output Control* button.

2. Select the *Print at specified times* option.

3. Select the *Times* button.

4. Select the *Initialize Values* button.

5. Enter 73.0 for the *Initial time step size*.

6. Enter 73.0 for the *Maximum time step size*.

7. Enter 730.0 for the *Maximum simulation time*.

8. Select the *OK* button to exit the *Initialize Time Steps* dialog.

9. Select the *Close* button to exit the *Variable Time Steps* dialog.

10. Select the *Close* button to exit the *Output Control* dialog.

This completes the input for the Basic Transport package.

Select the *Close* button to exit the *Basic Transport Package* dialog.

7.9   Assigning Concentrations to the Left Boundary

The left boundary of the model is a constant head boundary. Since the head at the left boundary is greater than the head at the right boundary, the left boundary acts as a source and water enters the model from the left. Thus, we must define the concentrations of our species at the left boundary. The simplest way to do this is to mark the cells as specified concentration cells.

1. Select the *Select Cell* tool

2. Select the cells on the left boundary by dragging a box that just surrounds the cells.

3. Select the *Cell Attributes* command in the *MT3D* menu.

4. Change the *ICBUND* value to –1.

5.   Select the *OK* button.

7.10   The Advection Package

The next step is to initialize the data for the Advection package.

1.   Select the *Advection Package* command from the *MT3D* menu.

2.   Select the *Method of characteristics* option.

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

7.11   The Dispersion Package

Next, we will enter the data for the Dispersion package. The aquifer has a longitudinal dispersivity of 10.0 m and a transverse (horizontal) dispersivity of 3.0 m.

1.   Select the *Dispersion Package* command in the *MT3D* menu.

2.   Select the *Longitudinal Dispersivity* button.

3.   Select the *Constant -> Grid* button.

4.   Enter a value of 10.0 and select *OK*.

5.   Enter a value of 0.3 for the *Ratio of the trans. dispersivity to long. dispersivity* value.

6.   Select the *Close* button to exit the *Dispersion Package* dialog.

7.12   The Source/Sink Mixing Package

Next, we will initialize the Source/Sink Mixing package and define the concentration at the spill location. We will assign a concentration of 500 mg/L for the electron donor and leave the other concentrations at the default value of 0.0.

1.   Select the *Source/Sink Mixing Package* command in the *MT3D* menu.

2.   In the *Initialize Point Source/Sinks from MODFLOW* section in the lower right corner of the dialog, select the *Well* button.

3.   Using the horizontal scroll bar below the spreadsheet section, scroll over until the *Electron Donor* column is visible.

4. Change the *Electron Donor* value to 500.0.

5. Select the *OK* button to exit the *Source/Sink Mixing Package* dialog.

7.13   The Chemical Reaction Package

Next, we will initialize the Chemical Reaction package and define appropriate reaction rate constants.

1. Select the *Chemical Reaction Package* command in the *MT3D* menu.

2. In the *Reaction Parameters* section, click on the *umax* item and set its value to 0.125.

3. Likewise, set the value of *Yea/ed* to 3.0.

The rest of the constants will all be left at the default values.

Select the *OK* button.

7.14   Running RT3D

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

1. Select the *Save As* command from the *MT3D* menu.

2. In the *Save As* dialog, change the path to the directory entitled *tutorial\rt3d\monod*.

3. Enter "bacteria" for the file name.

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

To run RT3D:

1. Select the *Run RT3D* command from the *MT3D* menu.

2. Select *OK* at the prompt.

3. When the simulation is finished, close the window and return to GMS.

7.15   Viewing the Results

Now, we will read in the concentration files and view the results.

1. Select the *Read Solution* command from the *MT3D* menu.

2. Select the *OK* button at the prompt.

7.15.1 Electron Donor

First, we will view the Electron Donor solution at 730 days.

1. Select the *Electron Donor* data set from the *Data Set* combo box.

2. Select the time step at t=730 days from the *TS* combo box.

To display color-filled contours:

1. Select the *Contour Options* command in the *Data* menu.

2. Turn on the *Color fill between contours* option.

3. Select the *OK* button.

Recall that the electron donor solution represents the contaminant. The plume is moving from the left to the right side, as expected.

7.15.2 Electron Acceptor

Next, we will view the electron acceptor solution.

Select the *Electron Acceptor* data set from the *Data Set* combo box.

Note that the electron acceptor solution is the inverse of the electron donor solution. The minimum value (the blue region) corresponds to the location of the plume.

7.15.3 Aqueous-Phase Bacteria

Next, we will view the solution for the aqueous-phase bacteria.

Select the *Aqueous phase bacteria* data set from the *Data Set* combo box.

Note that the bacteria are flourishing at the left end and around the edges of the plume where there is a combination of electron donors and electron acceptors.

7.15.4 Solid-Phase Bacteria

Finally, we will view the solid-phase bacteria. However, before viewing the data set, we need to adjust the data set. The mass fraction unit used for

representing soil bacterial cells (mg of bacteria/mg of soil) always yields small numbers. The resulting concentrations are so small that they sometimes produce numerical round-off errors in the GMS contouring routines. Thus, we will first utilize the *Data Calculator* to convert to units of mg/L. For example, assuming $\rho = 1.6 \times 10^6$ mg/L and $\phi = 0.3$, the initial value of soil bacterial concentration can be converted to liquid volume basis using the formula: $\widetilde{X} \rho/\phi$.

1. Select the *Data Calculator* command from the *Data* menu.

2. Enter "e*(1.6*10^6)/0.3" in the *Expression* field (the *Soil-Phase Bacteria* data set should be listed as item *e*).

3. Enter "Soil Bacteria" in the *Result* field.

4. Select the *Compute* button.

5. Select the *Done* button.

Note that the distribution of the soil bacteria is similar to the distribution of the aqueous-phase bacteria.

7.15.5   Other Post-Processing Options

At this point, you may wish to experiment with the other post-processing options, including film loop animation and time series plots.

7.16   Conclusion

This concludes the tutorial: *Double Monod Model*. If you wish to exit GMS at this time:

1. Select the *Exit* command from the *File* menu.

2. Select the *No* button at the prompt.