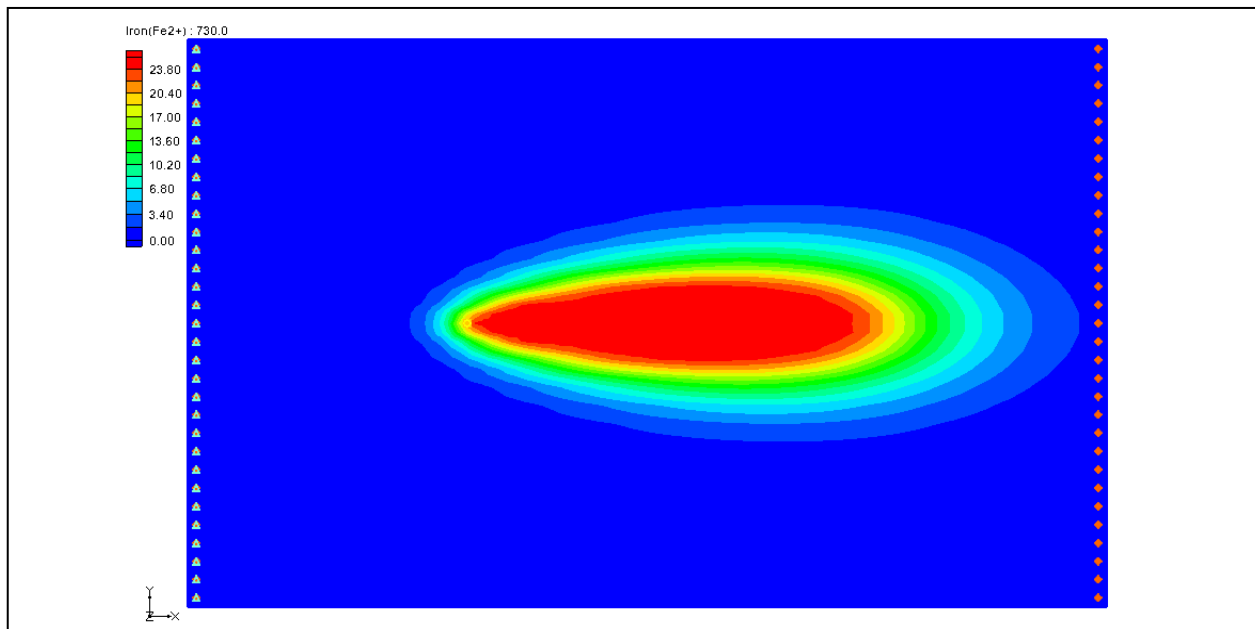


## GMS 10.0 Tutorial

### **RT3D – BTEX Degradation with Multiple Electron Acceptors**



#### Objectives

Use GMS and RT3D to model BTEX degradation using a multiple electron acceptor model.

#### Prerequisite Tutorials

- RT3D – Instantaneous Aerobic Degradation

#### Required Components

- Grid Module
- MODFLOW
- RT3D

#### Time

- 20-35 minutes



<b>1</b>	<b>Introduction</b> .....	<b>2</b>
1.1	Outline.....	2
<b>2</b>	<b>Description of the Reaction Model</b> .....	<b>2</b>
<b>3</b>	<b>Description of Problem</b> .....	<b>5</b>
<b>4</b>	<b>Getting Started</b> .....	<b>6</b>
<b>5</b>	<b>Importing the MODFLOW Model</b> .....	<b>6</b>
<b>6</b>	<b>Building the Transport Model</b> .....	<b>6</b>
<b>7</b>	<b>Initializing the Model</b> .....	<b>6</b>
<b>8</b>	<b>The BTN Package</b> .....	<b>7</b>
8.1	Starting Concentrations .....	7
8.2	Porosity .....	7
8.3	Stress Periods .....	8
8.4	Output Options .....	8
<b>9</b>	<b>Assigning Concentrations to the Left Boundary</b> .....	<b>9</b>
<b>10</b>	<b>The Advection Package</b> .....	<b>9</b>
<b>11</b>	<b>The Dispersion Package</b> .....	<b>9</b>
<b>12</b>	<b>The Source/Sink Mixing Package</b> .....	<b>10</b>
<b>13</b>	<b>The Chemical Reaction Package</b> .....	<b>10</b>
<b>14</b>	<b>Running RT3D</b> .....	<b>11</b>
<b>15</b>	<b>Viewing the Results</b> .....	<b>11</b>
15.1	Overlaying Contours .....	12
<b>16</b>	<b>Other Post-Processing Options</b> .....	<b>13</b>
<b>17</b>	<b>Conclusion</b> .....	<b>13</b>

## 1 Introduction

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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 the “RT3D – Instantaneous Aerobic Degradation” tutorial, 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.

### 1.1 Outline

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Here are the steps for this tutorial:

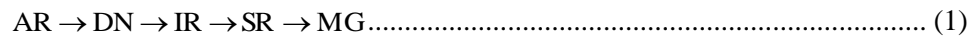
1. Import a MODFLOW model.
2. Define RT3D inputs and boundary conditions.
3. Run RT3D.
4. View results by overlaying the contours.

## 2 Description of the Reaction Model

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The reaction that the user 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:



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

$$r_{\text{HC},\text{O}_2} = -k_{\text{HC},\text{O}_2} [\text{HC}] \frac{[\text{O}_2]}{K_{\text{O}_2} + [\text{O}_2]} \dots \dots \dots (2)$$

$$r_{\text{HC},\text{NO}_3} = -k_{\text{HC},\text{NO}_3} [\text{HC}] \frac{[\text{NO}_3]}{K_{\text{NO}_3} + [\text{NO}_3]} \cdot \frac{K_{i,\text{O}_2}}{K_{i,\text{O}_2} + [\text{O}_2]} \dots \dots \dots (3)$$

$$r_{\text{HC},\text{Fe}^{3+}} = -k_{\text{HC},\text{Fe}^{3+}} [\text{HC}] \frac{[\text{Fe}^{3+}]}{K_{\text{Fe}^{3+}} + [\text{Fe}^{3+}]} \cdot \frac{K_{i,\text{O}_2}}{K_{i,\text{O}_2} + [\text{O}_2]} \dots \dots \dots (4)$$

$$\cdot \frac{K_{i,\text{NO}_3}}{K_{i,\text{NO}_3} + [\text{NO}_3]}$$

$$r_{\text{HC},\text{SO}_4} = -k_{\text{HC},\text{SO}_4} [\text{HC}] \frac{[\text{SO}_4]}{K_{\text{SO}_4} + [\text{SO}_4]} \cdot \frac{K_{i,\text{O}_2}}{K_{i,\text{O}_2} + [\text{O}_2]} \dots \dots \dots (5)$$

$$\cdot \frac{K_{i,\text{NO}_3}}{K_{i,\text{NO}_3} + [\text{NO}_3]} \cdot \frac{K_{i,\text{Fe}^{3+}}}{K_{i,\text{Fe}^{3+}} + [\text{Fe}^{3+}]}$$

$$r_{\text{HC},\text{CH}_4} = -k_{\text{HC},\text{CH}_4} [\text{HC}] \frac{[\text{CO}_2]}{K_{\text{CH}_4} + [\text{CO}_2]} \cdot \frac{K_{i,\text{O}_2}}{K_{i,\text{O}_2} + [\text{O}_2]} \dots \dots \dots (6)$$

$$\cdot \frac{K_{i,\text{NO}_3}}{K_{i,\text{NO}_3} + [\text{NO}_3]} \cdot \frac{K_{i,\text{Fe}^{3+}}}{K_{i,\text{Fe}^{3+}} + [\text{Fe}^{3+}]} \cdot \frac{K_{i,\text{SO}_4}}{K_{i,\text{SO}_4} + [\text{SO}_4]}$$

where  $r_{\text{HC},\text{O}_2}$  is the rate at which hydrocarbon is destroyed by utilizing oxygen,  $r_{\text{HC},\text{NO}_3}$  is the rate at which hydrocarbon is destroyed by utilizing Nitrate,  $r_{\text{HC},\text{Fe}^{2+}}$  is the rate at which hydrocarbon is destroyed by producing  $\text{Fe}^{2+}$  (or utilizing  $\text{Fe}^{3+}$ ),  $r_{\text{HC},\text{SO}_4}$  is the rate at which hydrocarbon is destroyed by utilizing sulfate,  $r_{\text{HC},\text{CH}_4}$  is the rate at which hydrocarbon is destroyed by producing methane,  $[\text{O}_2]$  is the oxygen concentration  $[\text{ML}^{-3}]$ ,  $k_{\text{O}_2}$  is the first-order rate constant  $[\text{T}^{-1}]$ ,  $K_{\text{O}_2}$  is the Monod half saturation constant  $[\text{ML}^{-3}]$  (by setting all the half-saturation constants to a small value, the user 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  $K_{i,\text{O}_2}$  is the oxygen inhibition constant  $[\text{ML}^{-3}]$  (by setting all inhibition constants to a small value, the user 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  $\text{Fe}^{3+}$  and  $\text{CO}_2$  are not readily measurable under normal field conditions, these terms were replaced with the “assimilative capacity” for iron reduction and methanogenesis, defined as the following:

$$[\text{Fe}^{3+}] = [\text{Fe}^{2+}_{\text{max}}] - [\text{Fe}^{2+}] \dots\dots\dots (7)$$

$$[\text{MC}] = [\text{CO}_2] = [\text{CH}_{4,\text{max}}] - [\text{CH}_4] \dots\dots\dots (8)$$

where  $[\text{Fe}^{2+}_{\text{max}}]$  and  $[\text{CH}_{4,\text{max}}]$  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  $\text{CO}_2$  used here is the  $\text{CO}_2$  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  $\text{Fe}^{2+}$  and  $\text{CH}_4$  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 the following:

$$\frac{d[\text{HC}]}{dt} = r_{\text{HC},\text{O}_2} + r_{\text{HC},\text{NO}_3} + r_{\text{HC},\text{Fe}^{2+}} + r_{\text{HC},\text{SO}_4} + r_{\text{HC},\text{CH}_4} \dots\dots\dots (9)$$

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

$$\frac{d[\text{O}_2]}{dt} = Y_{\text{O}_2/\text{HC}} r_{\text{HC},\text{O}_2} \dots\dots\dots (10)$$

$$\frac{d[\text{NO}_3]}{dt} = Y_{\text{NO}_3/\text{HC}} r_{\text{HC},\text{NO}_3} \dots\dots\dots (11)$$

$$\frac{d[\text{Fe}^{2+}]}{dt} = -Y_{\text{Fe}^{2+}/\text{HC}} r_{\text{HC},\text{Fe}^{2+}} \dots\dots\dots (12)$$

$$\frac{d[\text{SO}_4]}{dt} = Y_{\text{SO}_4/\text{HC}} r_{\text{HC},\text{SO}_4} \dots\dots\dots (13)$$

$$\frac{d[\text{CH}_4]}{dt} = -Y_{\text{CH}_4/\text{HC}} r_{\text{HC},\text{CH}_4} \dots\dots\dots (14)$$

The yield values (the mass ratio of electron acceptors removed or metabolic byproducts produced to total BTEX degraded) are as follows:  $Y_{\text{O}_2/\text{HC}} = 3.14$ ,  $Y_{\text{NO}_3/\text{HC}} = 4.9$ ,  $Y_{\text{Fe}^{2+}/\text{HC}} = 21.8$ ,  $Y_{\text{SO}_4/\text{HC}} = 4.7$ , and  $Y_{\text{CH}_4/\text{HC}} = 0.78$ . Typical values of all inhibition coefficients, except for  $K_{\text{Fe}^{3+}}$ , should be in the range of 1.0 to 0.01 mg/L.  $K_{\text{Fe}^{3+}}$  should always be set

around 40% to 80% of the max  $\text{Fe}^{2+}$  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.,<sup>1</sup> 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  $\text{Fe}^{2+}$  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 are not considered; these include processes such as the rate-limited interaction of bioavailable, solid-phase  $\text{Fe}^{3+}$  and aqueous-phase  $\text{Fe}^{2+}$ , interaction of oxygen and  $\text{Fe}^{2+}$ , and/or variations in the spatial pattern of methanogenic activity and  $\text{CO}_2$  availability; (4) growth and decay of various microbial populations and their interactions with contaminants and aquifer solids are assumed to be negligible; and (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 Description of Problem

The problem in this tutorial is the same as the problem described in “RT3D – Instantaneous Aerobic Degradation” tutorial. 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<sup>3</sup>/day at the location shown. Concentration of BTEX is 1000 mg/L. Initial levels of hydrocarbon, oxygen, nitrate,  $\text{Fe}^{2+}$ , sulfate, and methane in the aquifer are assumed to be as follows: 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 $\text{Fe}^{2+}$	25.0 mg/L
Max Methane	30.0 mg/L
$k_{\text{HC},\text{O}_2}$	0.1 day <sup>-1</sup>
$k_{\text{HC},\text{NO}_3}$	0.008 day <sup>-1</sup>
$k_{\text{HC},\text{Fe}^{3+}}$	0.0005 day <sup>-1</sup>
$k_{\text{HC},\text{SO}_4}$	0.00025 day <sup>-1</sup>
$k_{\text{HC},\text{CH}_4}$	0.0001 day <sup>-1</sup>

Values of all inhibition coefficients, except  $K_{\text{Fe}^{3+}}$ , are assumed to be 0.01 mg/L and all Monod constants are assumed to 0.5 mg/L. The value of  $K_{\text{Fe}^{3+}}$  is set at 12.5 mg/L (50% of max Fe). The yield values are the same as those described in the previous section.

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<sup>1</sup> Lu, G., Clement, T.P., Zheng, C., and Wiedemeier, T.H. (1999). Natural attenuation of BTEX compounds: Model development and field-scale application. *Ground Water*. 37(5):707–717.

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 Getting Started

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Do the following to get started:

1. If GMS is not running, launch GMS.
2. If GMS is already running, select the *File* / **New** command to ensure the program settings are restored to the default state.

## 5 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. Select the *File* | **Open** command.
2. Locate the directory entitled *Tutorials\RT3D\flowmod*.
3. Select the file entitled “flowmod.gpr.”
4. Click **Open**.

## 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, the user will select the reaction, define the reaction data, define the supplemental layer data needed by RT3D, and assign concentrations to the well.

## 7 Initializing the Model

---

The first step is to initialize the RT3D data.

5. Expand the “3D Grid Data” folder in the Project Explorer.
6. Right-click on the “grid”  item in the Project Explorer.
7. Select the **New MT3D...** command.

## 8 The BTN Package

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

1. In the *Model* section, select the *RT3D* option.
2. Select the **Packages** button to open the *MT3D/RT3D Packages* dialog.
3. Select the following packages:
  - Advection Package
  - Dispersion Package
  - Source/Sink Mixing Package
  - Chemical Reaction Package.
4. For the RT3D reactions, select the “Kinetic-Limited Deg. of BTEX w/ MEA” option.
5. Select the **OK** button to exit the *MT3D/RT3D Packages* dialog.

### 8.1 Starting Concentrations

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Note that in the *Layer Data* section of the dialog, the species associated with the reaction being modeled are listed by name. The next step is to define the starting concentration for each of these species. The default starting concentration is zero. The user will use the default value for BTEX,  $\text{Fe}^{2+}$ , and methane, but the user 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 in the spread sheet.
2. Enter a value of “4.0” for the starting concentration.
3. Enter a starting value of “20.0” for *Nitrate*.
4. Enter a starting value of “10.0” for *Sulfate*.

### 8.2 Porosity

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The porosity to be used is 0.3. Since this is the default in GMS, nothing needs to be changed.

### 8.3 Stress Periods

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

1. Select the **Stress Periods** button to open the *Stress Periods* dialog.
2. Enter a value of “730” for the *Length*.
3. Enter a value of “10” for the *Number of time steps*.
4. Select the **OK** button to exit the *Stress Periods* dialog.

### 8.4 Output Options

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Finally, the user 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 needed for the simple post-processing, the user will specify that a solution be saved every 73 days (every time step).

1. Select the **Output Control...** button to open the *Output Control* dialog.
2. Select the *Print or save at specified times* option.
3. Select the **Times** button to open the *Variable Time Steps* dialog.
4. Select the **Initialize Values** button to open the *Initialize Time Steps* dialog.
5. Enter “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.


11. Select the **OK** button to exit the *Basic Transport Package* dialog.



## 9 Assigning Concentrations to the Left Boundary

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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, the user must define the concentrations of the 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. Right-click on any of the selected cells.
4. Select the **Properties...** command from the pop-up menu to open the *3D Grid Cell Properties* dialog.
5. Switch to the *RT3D* tab.
6. Change the *ICBUND* value to **-1**.
7. Select the **OK** button.

## 10 The Advection Package

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

1. Select the *RT3D* | **Advection Package** command to open the *Advection Package* dialog.
2. Select the “Standard finite-difference method” solver from the *Solution scheme* drop-down menu of the dialog.
3. Select the **OK** button.

## 11 The Dispersion Package

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Next, the user 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 *RT3D* | **Dispersion Package** command to open the *Dispersion Package* dialog.
2. Select the **Longitudinal Dispersivity** button to open the *Longitudinal Dispersivity* dialog.

3. Select the **Constant** → **Grid** button to open the *Grid Value* dialog.
4. Enter a value of “10.0.”
5. Select **OK**.
6. Select the **OK** button to exit the *Longitudinal Dispersivity* dialog.
7. Enter a value of “0.3” for the *TRPT* value.
8. Select the **OK** button to exit the *Dispersion Package* dialog.

## 12 The Source/Sink Mixing Package

---

Next, the user will define the concentration at the spill location. The user 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 cell containing the injection well (spill location) by clicking anywhere in the interior of the cell.
2. Select the *RT3D* | **Point Sources/Sinks** command.
3. Click the **Add BC** button near the bottom of the dialog.
4. Change the *Type (ITYPE)* to “well (WEL).”
5. In the *BTEX* column, enter a concentration of “1000” (mg/L).
6. Select the **OK** button to exit the dialog.

## 13 The Chemical Reaction Package

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

1. Select the *RT3D* / **Chemical Reaction Package** command.
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  $k_{\text{HC},\text{O}_2}$  to “0.1.”
5. Set the value of  $k_{\text{HC},\text{NO}_3}$  to “0.008.”
6. Set the value of  $k_{\text{HC},\text{Fe}^{3+}}$  to “0.0005.”

7. Set the value of  $k_{\text{HC,SO}_4}$  to “0.00025.”
8. Set the value of  $k_{\text{HC,CH}_4}$  to “0.0001.”

All monod constants inhibition coefficients, and yield values, except  $K_{\text{Fe}^{3+}}$ , will be left at the default values. The value of  $K_{\text{Fe}^{3+}}$  is set at 12.5 mg/L (50% of max Fe).

9. Set the value of  $K_{\text{Fe}^{3+}}$  to “12.5.”
10. Select the **OK** button.

## 14 Running RT3D

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

1. Select the *File* | **Save As** command.
2. In the *Save As* dialog, locate and open the directory entitled *Tutorials\RT3D\btexkin*.
3. Enter “btmod” for the file name.
4. Select the **Save** button.

Since the user has changed the name of the project, the user must either use *the Run Options* command to tell RT3D where the MODFLOW solution is, or re-run MODFLOW. The user will do the latter.

5. Select the *MODFLOW* | **Run MODFLOW** command.
6. When the simulation is finished, select the **Close** button.

To run RT3D:


7. Select the *RT3D* | **Run RT3D** command.
8. Select **Yes** at the prompt to save the changes.
9. When the simulation is finished, select the **Close** button.

GMS reads in the solution automatically.

## 15 Viewing the Results

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

1. Select the “BTEX”  dataset from the Project Explorer. (The user may need to expand the “btmod (RT3D)” solution in the Project Explorer.)


2. Select the time step at 730 days from the *Time Steps Window*.

## 15.1 Overlaying Contours

---

Next, the user 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, the user will overlay the contours of the other species on top of the BTEX contours. To do this, the user must display the BTEX contours in the background as a CAD layer.


Before creating the CAD layer, the user will turn off most of the display options other than the contours (to avoid saving the grid cell lines to the CAD file).

1. Select the **Display Options**  macro.
2. Turn off the *Cells edges* option.
3. Switch to the *RT3D* tab
4. Select the **Check None** button.
5. Switch to the *MODFLOW* tab.
6. Select the **Check None** button.
7. Select **OK**.

To create the CAD layer:

8. In the Project Explorer, right-click on the empty space.
9. Then, from the pop-up menu, select the **Convert to CAD** command.
10. In the *Save CAD Data* dialog, enter “BTEX\_contours” as the file name.
11. Select **Save**.

The user will now reset the display options and view the oxygen solution at 730 days.


12. Select the **Display Options**  macro.
13. Turn on the *Layer Borders* option.
14. Select the **OK** button.
15. Select the *Oxygen* dataset from the Project Explorer.

The user will also turn on a color ramp and a legend.

16. Select the **Contour Options**  macro.

17. Select the “Color Fill” option for the *Contour Method*.
18. Change the *Transparency* value to “50.”
19. Select the **OK** button to exit the *Contour Options* dialog.
20. Select the time step at 730 days from the *Time Steps Window*.

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

21. Select the “Nitrate”  dataset from the Project Explorer.
22. Select the time step at 730 days from the *Time Steps Window*.

Finally, the user will view the Fe<sup>2+</sup> solution at 730 days.

23. Select the “Iron (Fe<sup>2+</sup>)”  dataset from the Project Explorer.
24. Select the time step at 730 days from the *Time Steps Window*.

## 16 Other Post-Processing Options

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

## 17 Conclusion

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This concludes the tutorial.