

GMS TUTORIALS

RT3D – 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 *RT3D – 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.

1.1 Outline

This is what you will do:

1. Import a MODFLOW model.
2. Define conditions.
3. Run MT3D.
4. View results by overlaying the contours.

1.2 Required Modules/Interfaces

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

- Grid
- MODFLOW
- RT3D and ART3D

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

2 Description of the Reaction Model

The 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:



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

$$r_{HC,O_2} = -k_{HC,O_2} [HC] \frac{[O_2]}{K_{O_2} + [O_2]} \dots\dots\dots (2)$$

$$r_{HC,NO_3} = -k_{HC,NO_3} [HC] \frac{[NO_3]}{K_{NO_3} + [NO_3]} \cdot \frac{K_{i,O_2}}{K_{i,O_2} + [O_2]} \dots\dots\dots (3)$$

$$r_{HC,Fe^{3+}} = -k_{HC,Fe^{3+}} [HC] \frac{[Fe^{3+}]}{K_{Fe^{3+}} + [Fe^{3+}]} \cdot \frac{K_{i,O_2}}{K_{i,O_2} + [O_2]} \dots\dots\dots (4)$$

$$\cdot \frac{K_{i,NO_3}}{K_{i,NO_3} + [NO_3]}$$

$$r_{HC,SO_4} = -k_{HC,SO_4} [HC] \frac{[SO_4]}{K_{SO_4} + [SO_4]} \cdot \frac{K_{i,O_2}}{K_{i,O_2} + [O_2]} \dots\dots\dots (5)$$

$$\cdot \frac{K_{i,NO_3}}{K_{i,NO_3} + [NO_3]} \cdot \frac{K_{i,Fe^{3+}}}{K_{i,Fe^{3+}} + [Fe^{3+}]}$$

$$r_{HC,CH_4} = -k_{HC,CH_4} [HC] \frac{[CO_2]}{K_{CH_4} + [CO_2]} \cdot \frac{K_{i,O_2}}{K_{i,O_2} + [O_2]} \dots\dots\dots (6)$$

$$\cdot \frac{K_{i,NO_3}}{K_{i,NO_3} + [NO_3]} \cdot \frac{K_{i,Fe^{3+}}}{K_{i,Fe^{3+}} + [Fe^{3+}]} \cdot \frac{K_{i,SO_4}}{K_{i,SO_4} + [SO_4]}$$

where r_{HC,O_2} is the rate at which hydrocarbon is destroyed by utilizing oxygen, r_{HC,NO_3} is the rate at which hydrocarbon is destroyed by utilizing Nitrate, $r_{HC,Fe^{2+}}$ is the rate at which hydrocarbon is destroyed by producing Fe^{2+} (or utilizing Fe^{3+}), r_{HC,SO_4} is the rate at which hydrocarbon is destroyed by utilizing sulfate, r_{HC,CH_4} is the rate at which hydrocarbon is destroyed by producing methane, $[O_2]$ is the oxygen concentration $[ML^{-3}]$, k_{O_2} is the first-order rate constant $[T^{-1}]$, K_{O_2} 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,O_2} 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:

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

$$[MC] = [CO_2] = [CH_{4,max}] - [CH_4] \dots\dots\dots (8)$$

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:

$$\frac{d[HC]}{dt} = r_{HC,O_2} + r_{HC,NO_3} + r_{HC,Fe^{2+}} + r_{HC,SO_4} + r_{HC,CH_4} \dots\dots\dots (9)$$

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

$$\frac{d[O_2]}{dt} = Y_{O_2/HC} r_{HC,O_2} \dots\dots\dots (10)$$

$$\frac{d[NO_3]}{dt} = Y_{NO_3/HC} r_{HC,NO_3} \dots\dots\dots (11)$$

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

$$\frac{d[SO_4]}{dt} = Y_{SO_4/HC} r_{HC,SO_4} \dots\dots\dots (13)$$

$$\frac{d[CH_4]}{dt} = -Y_{CH_4/HC} r_{HC,CH_4} \dots\dots\dots (14)$$

The yield values (the mass ratio of electron acceptors removed or metabolic byproducts produced to total BTEX degraded) are: $Y_{O_2/HC} = 3.14$, $Y_{NO_3/HC} = 4.9$, $Y_{Fe^{2+}/HC} = 21.8$, $Y_{SO_4/HC} = 4.7$, and $Y_{CH_4/HC} = 0.78$. Typical values of all inhibition coefficients, except for $K_{iFe^{3+}}$, should be in the range of 1.0 to 0.01 mg/L. $K_{iFe^{3+}}$ 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 Fe^{2+} , 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 Description of Problem

The problem we will be solving in this tutorial is the same as the problem described in *RT3D – Instantaneous Aerobic Degradation*. 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 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 Fe^{2+}	25.0 mg/L
Max Methane	30.0 mg/L
k_{HC,O_2}	0.1 day ⁻¹
k_{HC,NO_3}	0.008 day ⁻¹
$k_{HC,Fe^{3+}}$	0.0005 day ⁻¹
k_{HC,SO_4}	0.00025 day ⁻¹
k_{HC,CH_4}	0.0001 day ⁻¹

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

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

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 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 and open the file entitled **tutfiles\RT3D\flowmod\flowmod.gpr**.

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.

7 Initializing the Model

The first step is to initialize the RT3D data.

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

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. In the *Model* section, select the *RT3D* option.
2. Select the *Packages* button.
3. Select the Advection Package, the Dispersion Package, the Source/Sink Mixing Package, and the 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 *Packages* dialog.

8.1 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. 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*.

8.2 Porosity

The porosity we will use is 0.3. Since this is the default in GMS, we don't need to do anything.

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 *Number of time steps*.
4. Select the *OK* button to exit the *Stress Periods* dialog.

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 or save 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.

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

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. Right-click on any of the selected cells, and select the *Properties...* command from the pop-up menu.
4. Switch to the *MT3D* tab.

5. Change the *ICBUND* value to **-1**.
6. Select the *OK* button.

10 The Advection Package

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

1. Select the *MT3D | Advection Package* command.
2. Select the *Standard finite-difference method* solver from the *Solution scheme* section of the dialog.
3. Select the *OK* button.

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 *MT3D | Dispersion Package* command.
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 *TRPT* value.
7. Select the *OK* button to exit the *Dispersion Package* dialog.

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 *MT3D | Source/Sink Mixing Package* command.
2. In the *Initialize Point Sources/Sinks from MODFLOW* section in the lower left 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.

13 The Chemical Reaction Package

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

1. Select the MT3D | 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_{HC,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 $k_{\text{HC},\text{SO}_4}$ to **0.00025**.
8. Set the value of $k_{\text{HC},\text{CH}_4}$ to **0.0001**.

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

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

14 Running RT3D

At this point, we are ready 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 *tutfiles\rt3d\btexkin*.
3. Enter "**btmod**" for the file name.
4. Select the *Save* button to save the files.

Since we've changed the name of the project, we must either use the *Run Options* command to tell RT3D where the MODFLOW solution is, or re-run MODFLOW. We'll 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 *MT3D | Run RT3D* command.
8. Select *Yes* at the prompt.
9. When the simulation is finished, select the *Close* button.

GMS reads in the solution automatically.

15 Viewing the Results


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

1. Select the *BTEX* data set  from the *Project Explorer*. (You 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, 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 display the BTEX contours in the background as a CAD layer.

Before creating the CAD layer, we 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 *MT3D* tab
4. Select the *Check None* button..
5. Switch to the *MODFLOW* tab.

6. Select the *Check None* button and hit *OK*.

To create the CAD layer:

7. In the *Project Explorer* right-click on the empty space and then, from the pop-up menu, select the *Convert to CAD* command.

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

8. Select the *Display Options* macro .
9. Turn on the *Layer Borders* option.
10. Select the *OK* button.
11. Select the *Oxygen* data set from the *Project Explorer*.

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

12. Select the *Data | Contour Options* command.
13. Select the **Color Fill** option for the *Contour Method*.
14. Select the *Color Ramp* button.
15. Select the *Legend* option.
16. Select the *OK* button to exit the *Color Ramp Options* dialog.
17. Select the *OK* button to exit the *Contour Options* dialog.
18. Select the time step at **730** days from the *Time Steps Window*.

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

19. Select the *Nitrate* data set  from the *Project Explorer*.
20. Select the time step at **730** days from the *Time Steps Window*.

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

21. Select the *Iron (Fe^{2+})* data set  from the *Project Explorer*.
22. Select the time step at **730** days from the *Time Steps Window*.

16 Other Post-Processing Options

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

17 Conclusion

This concludes the tutorial
