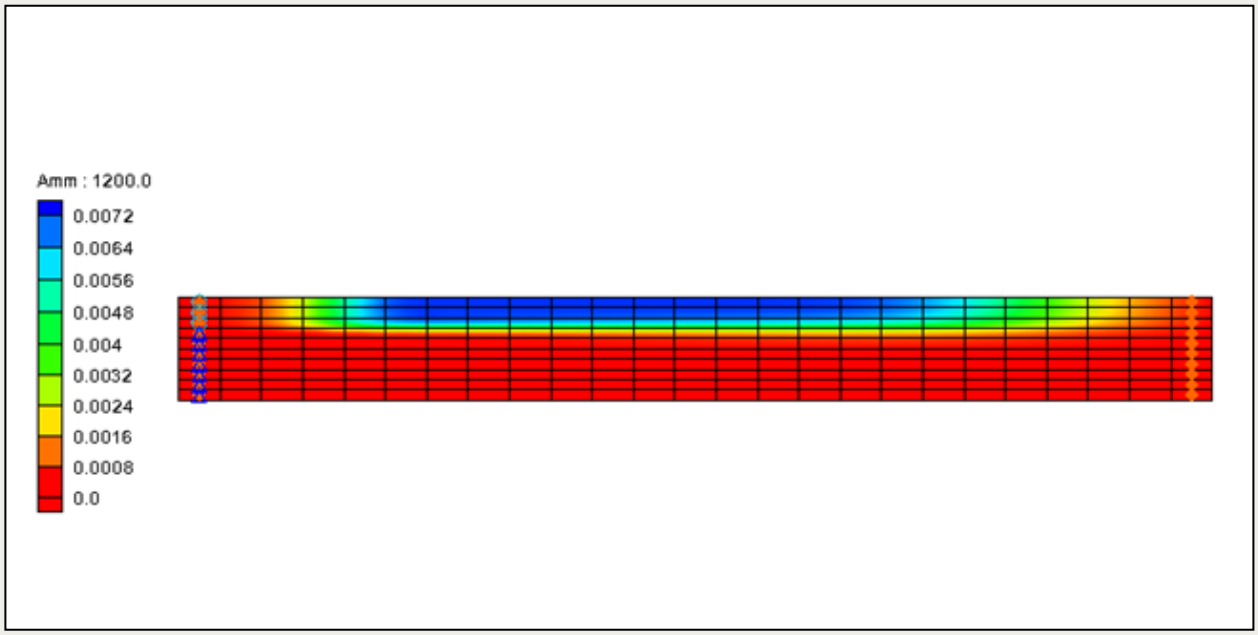
GMS 10.9 Tutorial

PHT3D – Ion Exchange and Surface Complexation

PHT3D Sorption processes



Objectives

This tutorial demonstrates ion exchange and surface complexation in PHT3D.

Prerequisite Tutorials

- MT3DMS – Grid Approach

Required Components

- GMS Core
- MODFLOW Interface
- MT3D
- PHT3D

Time

- 15–30 minutes

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1 Introduction

Sorption of species on the surface of solids is an important regulating mechanism for concentrations of dissolved ions in natural waters. Natural substances whose surfaces can act as sorbers include clay minerals, organic particles and oxides/hydroxides. The capability of reactive transport models to simulate sorption processes is essential to the successful application of these models.

When dealing with sorption processes, a distinction is often made between surfaces with a constant exchange capacity (ion exchange) and surfaces with a variable charge (surface complexation). In ion exchange problems, ions are adsorbed and released in equivalent proportions. The exchange capacity of the exchanging surface is assumed constant and the net charge of the surface does not change during the exchange on clay and organic surfaces.

In surface complexation, on the other hand, the charge of the surface is variable and dependent on the amount and kind of ions sorbed. It applies, for example, to sorption of heavy metals on the surface of oxides and hydroxides. PHT3D can simulate sorption through ion exchange and surface complexation.

1.1 Description of the Problem

This modeling example is based on a field site contamination problem near Mansfield, England, where ammonium liquor, a by-product of smokeless fuel production, has polluted groundwater over several decades. One of the key features observed at the site is the strongly retarded migration of ammonium and the geochemical footprint that was left behind as a result of the cation exchange of ammonium.

For simplicity, a two-dimensional reactive transport problem is set up. The simulation period is divided into two different stress periods. The first stress period represents the

period of active contamination during which the plume grows successively, while the second stress period represents the period after the source was exhausted.

2 Getting Started

Do the following to get started:

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

3 Importing the Flow Model

Before setting up the PHT3D simulation, it is necessary to have a MODFLOW solution that will be used as the flow field for the transport simulation. In the interest of time, import a previously created MODFLOW simulation.

1. Click **Open** to bring up the *Open* dialog.
2. Browse to the *IonExchange* directory and select "start.gpr".
3. Click **Open** to exit the *Open* dialog and import the project.

The flow model has already been created in this example (Figure 1).

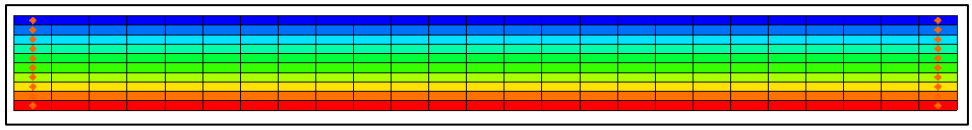

Figure 1 Flow model

3.1 Saving the Project with a New Name

Before continuing, save the project with a new name.

1. Select *File* | **Save As…** to open the *Save As* dialog.
2. Enter **"**pht3d_run1.gpr" as the *File name* and click **Save** to close the *Save As* dialog.

It is recommended to periodically save the project.

4 Building the Transport Model

With a flow solution, it is possible to set up the PHT3D transport simulation.

4.1 Initializing the Simulation

First, initialize the simulation.

1. Right-click in the blank area of the Project Explorer and select **Expand All**.
2. Right-click on "grid" and select **New MT3DMS…** to bring up the *Basic Transport Package* dialog.

3. In the *Model* section, select *PHT3D.*
4. Continue to the next section.

4.2 PHT3D Reaction Definition

In this tutorial, use an existing PHREEQC-2 database to define the reaction.

1. Click **Define Species…** to open the *PHT3D Options* dialog.

This dialog contains PHT3D general options and also allows for the defining of the species to be used. Notice that the first item available in the list box is *General Options*.

2. From the list on the left, select "Equilibrium Species".

Because a PHREEQC database has not yet been selected, candidate equilibrium species cannot be viewed. A PHREEQC database can be selected by doing the following:

3. Next to *PHREEQC database,* click **Open** to bring up the *Open* dialog.
4. Select "pht3d_datab.dat" and click **Open** to close the *Open* dialog and import the database.

GMS has now imported the PHREEQC database and made available the different components included in the file. Now select the components to model.

5. In the *Active* column in the spreadsheet, turn on:
   - *O(0)*
   - *Ca,*
   - *Mg*
   - *Na*
   - *K*
   - *Cl*
   - *C(4)*
   - *C(-4)*
   - *S(6)*
   - *N(5)*
   - *N(3)*
   - *N(0)*

Note that *pH* and *pe* species are automatically included in all simulations.

6. From the list on the left, select "Kinetic Species".
7. In the *Active* column, turn on *Amm*.
8. From the list on the left, select "Equilibrium Minerals/Phases".
9. In the *Active* columns, turn on *Calcite*.

The selection of species to include in the simulation is now completed.

10. Click **OK** to close the *PHT3D Options* dialog.

In the spreadsheet, scroll down and notice that the *pH* and *pe* species are in the list of species.

4.3 Initial Concentrations

The next step is to specify the initial concentrations that define the hydrogeochemistry of the aquifer at the start of the simulation (Time = 0).

1. In the spreadsheet, on the *O(0)* row, in the *Starting Conc. (moles/liter)* column, enter "0.000251".
2. Repeat step 1 for each of the species listed in Table 1 and Table 2, respectively.

This specifies the initial concentrations for all the aqueous components and minerals used in this tutorial project.

Table 1 Initial aqueous concentrations

Aqueous	Background and flushing water C_{backgr} , C_{flush} (mol/l)
Amm	0.0
O(0)	0.000251
Ca	0.00183
Mg	0.00138
Na	0.000862
K	0.000124
Cl	0.00174
C(4)	0.00282
C(-4)	0.0
S(6)	0.000989
N(5)	0.000888
N(3)	0.0
N(0)	0.0
pH	7.9
pe	13.5

Table 2 Initial mineral concentration

Mineral	C_{init} (mol/l_b)
Calcite	0.1

4.4 Packages

Next, select which packages to be used.

1. Click **Packages…** to open the *MT3DMS/RT3D Packages* dialog.
2. Turn on *Advection package*, *Dispersion package*, and *Source/Sink mixing package*.
3. Click **OK** to close the *MT3DMS/RT3D Packages* dialog.

4.5 Porosity Array

Finally, define the porosity for the cells. The problem has a constant porosity of 0.32.

1. Click **Porosity…** to open the *Porosity* dialog.
2. In the *Porosity* dialog, select **Constant** → **Grid…** to open the *Grid Value* dialog.
3. For the *Constant value for grid,* enter “0.32”.
4. Click **OK** to close the *Grid Value* dialog.
5. Click **OK t**o exit the *Porosity* dialog.
6. Click **OK** to exit the *Basic Transport Package* dialog.

4.6 Run Options

Next, tell MT3DMS to always use the same MODFLOW solution to define the flow field. This allows for the saving of the transport simulation under a different name without having to re-run MODFLOW.

1. Select *PHT3D* | **Run Options…** to open the *Run Options* dialog.
2. Select *Single run with selected MODFLOW solution*.
3. Click **OK** to close the *Run Options* dialog.

5 Advection Package

The simulation in this tutorial uses the default settings for the advection package, so nothing needs to be edited in the *Advection Package* dialog.

6 Dispersion Package

Now edit the inputs to the dispersion package. To enter the data for the dispersion package:

1. Select *PHT3D* | **Dispersion Package…** to open the *Dispersion Package* dialog.
2. Click **Longitudinal Dispersivity…** to open the *Longitudinal Dispersivity* dialog.
3. Click **Constant** → **Grid…** to open the *Grid Value* dialog.
4. For the *Constant value for grid,* enter “0.0067”.
5. Click **OK** to close the *Grid Value* dialog.
6. Click **OK** to exit the *Longitudinal Dispersivity* dialog.
7. Click **OK** to exit the *Dispersion Package* dialog.

7 Adding Inflow Concentration

The flow model has been set up with a constant head of 12 feet on the left of the model and a constant head of 10 feet on the right. The flow should move from left to right through the model grid. For the first stress period, contaminated water should only be entering the model from the top 3 left-most cells. The water from the bottom 7 left-most cells, called flushing water, should have the same concentrations with the initial concentration in the model.

7.1 Assigning Inflow Concentrations from Flushing Water

1. Using the **Select Cells** tool, while holding down the *Shift* key, select the bottom seven cells in the leftmost column (Figure 2).
2. Right-click on one of the cells and select **Properties…** to open the *3D Grid Cell Properties* dialog.
3. On the *PHT3D* tab, on the *ICBUND* row, in the *Value* column, enter “-1”.
4. Click **OK** to exit the *3D Grid Cell Properties* dialog.

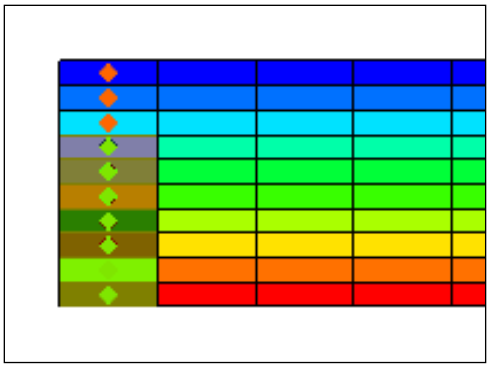

Figure 2 Bottom seven cells in the leftmost column selected

7.2 Assigning Inflow Concentrations from Contaminated Water

Now, assign the inflow concentrations of the contaminated water.

1. Using the **Select Cells** tool, while holding down the *Shift* key, select the top three cells in the leftmost column (Figure 3).

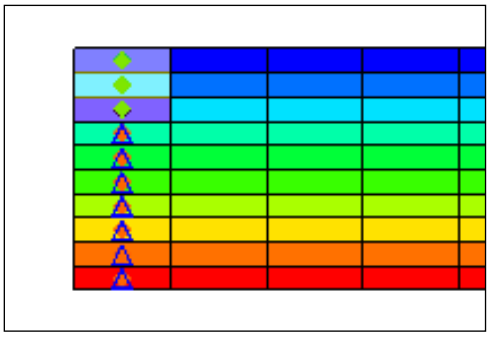

Figure 3 Top three cells in the leftmost column selected

2. Right-click on a cell and select **Sources/Sinks…** to open the *MODFLOW/PHT3D Sources/Sinks* dialog.
3. From the list on the left, select “PHT3D: Point SS”.
4. Click **Add BC** to create entries in the spreadsheet.

It is now possible to assign the inflow concentrations of the contaminated water for the first stress period. However, this is more easily accomplished using the *Source/Sink Mixing Package* dialog.

5. Click **OK** to exit the *MODFLOW/PHT3D Source/Sinks* dialog.
6. Click anywhere outside the project cells to deselect the cells.
7. Select *PHT3D* | **Source/Sink Mixing Package…** to *Source/Sink Mixing Package* dialog.

The *Stress period* in the *Point sources/sinks* section defaults to “1”. Notice the three new boundary conditions listed in the spreadsheet.

8. Enter the contaminated water concentration, listed in Table 3, for each species in all three rows.

Table 3 Aqueous component concentrations in contaminated water

Aqueous	Contaminated water C_{cont} (mol/l)
Amm	0.00687
O(0)	0
Ca	0.00015
Mg	0.00005
Na	0.0013
K	0.00013
Cl	0.00323
C(4)	0.00292
C(-4)	0
S(6)	0.00156
N(5)	0
N(3)	0
N(0)	0
pH	8.3
pe	0

9. Change the *Stress Period* to "2".
10. Enter the flushing water concentration, listed in Table 1 in section 4.3, for each species in all three rows. Do not enter the *Calcite* concentration from Table 2.
11. Click **OK** to exit the *Source/Sink Mixing Package* dialog.

8 Saving the Simulation and Running PHT3D

It is now possible to save the simulation and run PHT3D.

1. **Save** the project.
2. Select *MODFLOW* | **Run MODFLOW** to bring up the *MODFLOW* model wrapper dialog.
3. When *MODFLOW* finishes the simulation, turn on *Read solution on exit* and *Turn on contours (if not on already)* and click **Close** to exit the *MODFLOW* model wrapper dialog.
4. **Save** the project.
5. Select *PHT3D* | **Run PHT3D…** to bring up the *PHT3D* model wrapper dialog.
6. When *PHT3D* finishes, turn on *Read solution on exit* and click **Close** to exit the *PHT3D* model wrapper dialog.

9 Viewing the Solution

After PHT3D finished running, GMS automatically imported the computed concentrations, mass files, and output file produced by PHT3D.

1. If necessary, in the Project Explorer, expand the "pht3d_run1 (PHT3D)" folder.
2. Select the "Amm" dataset.
3. Below the Project Explorer, in the *Time Steps* window, select the first time step.
4. Use the arrow keys to view the different time steps.

Notice that the ammonium is flushed out of the system by time step 68.

9.1 Time Series Data Plot

Next, generate the time series data plot related to the concentrations.

1. Select the "N(5)" dataset.
2. Click **Plot Wizard** to open the *Step 1 of 2* page of the *Plot Wizard* dialog.
3. Under *Plot Type,* select "Active Dataset Time Series".
4. Click **Finish** to close the *Plot Wizard* dialog and bring up the *Active Dataset Time Series* dialog.
5. Using the **Select Cells** tool, select a cell in one of the top three layers near the middle of the model.

Select different species from the Project Explorer to see how the concentration of each species varies with time.

6. When finished reviewing the various species, close the *Active Dataset Time Series* dialog.

10 Ion Exchange Reactions

So far, this tutorial has not considered ion exchange reactions. To include ion exchange, it is necessary to include the cation species in the reaction network and define the initial concentrations on the exchanger site.

10.1 Defining Exchange Species

1. Select *PHT3D* | **Basic Transport Package…** to open the *Basic Transport Package* dialog.
2. Click **Define Species…** to open the *PHT3D Options* dialog.
3. From the list on the left, select "Exchange Species".
4. Turn off *Only show active species* so all species show in the spreadsheet.
5. In the *Active* column, turn on *NaX, KX, AmmHX, CaX2,* and *MgX2*.
6. Click **OK** to close the *PHT3D Options* dialog.

10.2 Defining Exchange Species Initial Concentrations

The next step is to specify the initial concentrations of these exchange species.

1. In the spreadsheet, scroll down to *CaX2*.
2. In the *Starting Conc. (moles/liter)* column, enter "0.03363".
3. Repeat steps 1 and 2 for each of the species in Table 4.

Table 4 Exchange Species

Exchange Species	Concentration C_{init} (mol/l)
KX	0.00000266
AmmHX	0
NaX	0.000006276
MgX2	0.02637

This specifies the initial concentrations for these exchange species.

4. Click **OK** to close the *Basic Transport Package* dialog.

11 Saving the Simulation and Running PHT3D

It is now possible to save the simulation under a different name and run PHT3D.

1. Select *File* | **Save As…** to open the *Save As* dialog.
2. Enter "pht3d_run2.gpr" as the *File name* and click **Save** to close the *Save As* dialog.
3. Select *PHT3D* | **Run PHT3D…** to bring up the *PHT3D* model wrapper dialog.
4. When the *PHT3D* simulation is finished, turn on *Read solution on exit* and click the **Close** to exit the *PHT3D* model wrapper dialog.

12 Viewing the Solution

After PHT3D finished running, GMS imported the computed concentrations, mass files, and output file produced by PHT3D. To view the solution data, do the following:

1. If necessary, in the Project Explorer, expand "  pht3d_run2 (PHT3D)".
2. Select the "  AmmHX" dataset.
3. Below the Project Explorer, in the *Time Steps* window, select the first time step.
4. Use the arrow keys to view the different time steps.

Feel free to select different exchange species datasets from the Project Explorer to see how the concentrations vary with time.

13 Conclusion

This concludes the “PHT3D – Ion Exchange and Surface Complexation” tutorial. The following key concepts were discussed and demonstrated in this tutorial:

- How to define species in PHT3D using the original PHREEQC-2 database.
- How to specify the concentrations for a particular species.
- How to create boundary conditions with different concentrations for different stress periods.
- How to define exchange species.