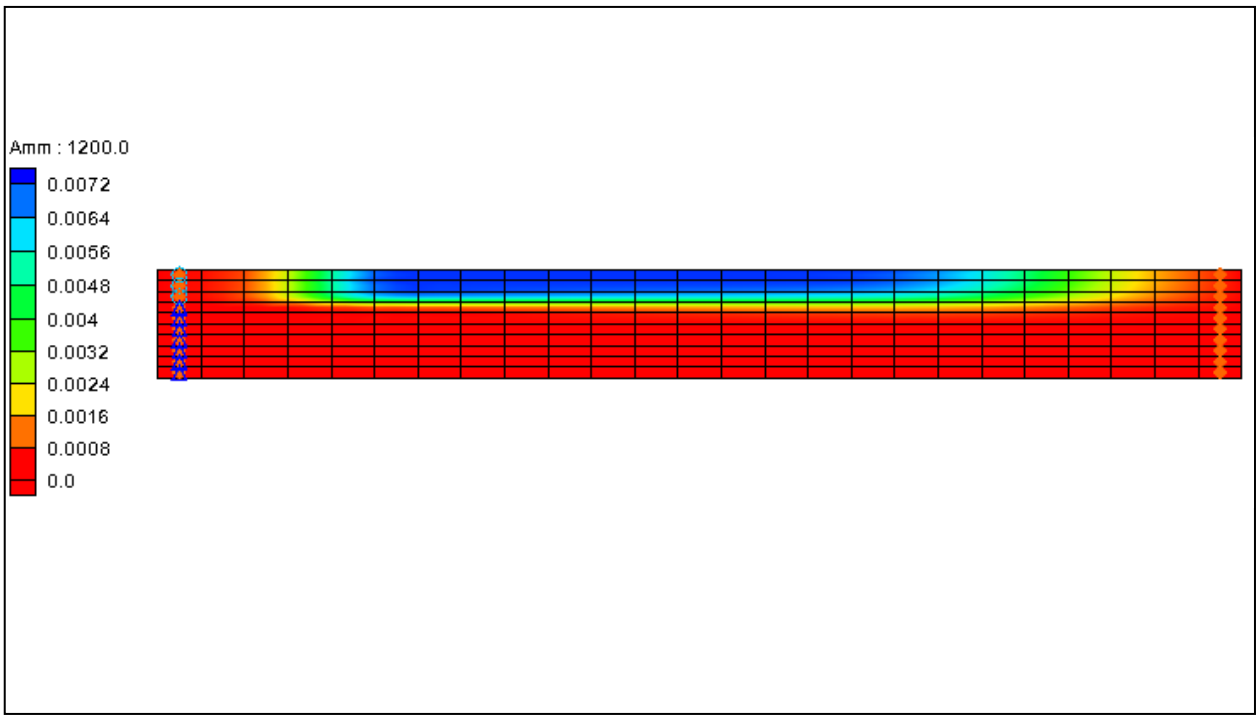
GMS 10.0 Tutorial

PHT3D – Ion Exchange and Surface Complexation

PHT3D Sorption processes



Objectives

Learn about ion exchange and surface complexation in PHT3D.

Prerequisite Tutorials

- MT3DMS - Grid Approach

Required Components

- Grid Moduule
- MODFLOW
- MT3D
- PHT3D

Time

- 25-40 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. PHREEQC-2 can simulate sorption through ion exchange and surface complexation.

2 Description of Problem

This modeling example is based on a field site contamination problem near Mansfield, UK, where ammonium liquor, a by-product of smokeless fuel production, has polluted

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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.

3 Getting Started

Do the following to get started:

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

4 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, the user will read in a previously created MODFLOW simulation.

1. Select the **Open** button.
2. Locate and open the directory entitled *Tutorials\PHT3D\IonExchange*.
3. Select the file entitled "start.gpr."
4. Select the **Open** button.

The flow model has already been created in this example.

5 Save the Project With a New Name

Before continuing, save the project with a new name.

1. Select the *File* | **Save As** command.
2. Change the project name to **"**pht3d_run1.gpr."
3. Click **Save.**

It's a good idea to save the work periodically.

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6 Building the Transport Model

Now that the user has a flow solution, it is possible to set up the PHT3D transport simulation.

6.1 Initializing the Simulation

First, the user will initialize the simulation.

1. Expand the items in the Project Explorer.
2. Right-click on the "grid" item.
3. Select the **New MT3D** command.
4. Under the *Model* section in the dialog, select *PHT3D.*

6.2 PHT3D Reaction Definition

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

1. Select the **Define Species** button to open the *Define Species* dialog.

This dialog allows the user to define the species that the user will use as well as PHT3D general options. Notice that the first item available in the list box is *General Options.*

2. Select *Equilibrium Species* from the list box on the left of the dialog.

The user is unable to view any candidate equilibrium species because the user has not yet selected a PHREEQC database. The user will select a PHREEQC database now.

3. Select the **Open** button next to *PHREEQC database*.
4. Locate and open the directory entitled *Tutorials\PHT3D\IonExchange*.
5. Select the file entitled "pht3d_datab.dat."
6. Select the **Open** button.

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

7. Select the *Equilibrium Species* option in the left window.
8. Turn on the *Active* check box in the spreadsheet window for the following: *O(0), Ca, Mg, Na, K, Cl, C(4), C(-4), S(6), N(5), N(3),* and *N(0)*. Note that the user will not explicitly select *pH* and *pe* because these species are automatically included in all simulations.

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9. Select the *Kinetic Species* option in the left window.
10. Turn on the *Active* check box in the right window for *Amm*.
11. Select the *Equilibrium Minerals/Phases* option in the left window.
12. Turn on the *Active* check box in the right window for *Calcite*.

The user is now done selecting the species to include in the simulation; the user will accept the other default options in the dialog.

13. Select the **OK** button.

6.3 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 spread sheet, select the *O(0) Species.*
2. Enter "0.000251" for the concentration.

Use the same procedures described above to specify the initial concentrations for all the aqueous aqueous components and minerals listed in Table 1and

Table 2, respectively.

Table 1 Initial aqueous concentrations used in this tutorial

Aqueous	**Background and flushing water** C_{backgr} , C_{flush} (mol/l)
Amm	0.0
O(0)	2.51×10^{-4}
Ca	1.83×10^{-3}
Mg	1.38×10^{-3}
Na	8.62×10^{-4}
K	1.24×10^{-4}
Cl	1.74×10^{-3}
C(4)	2.82×10^{-3}
C(-4)	0.0
S(6)	9.89×10^{-4}
N(5)	8.88×10^{-4}
N(3)	0.0
N(0)	0.0
pH	7.9
pe	13.5

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Table 2 Initial mineral concentration

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

6.4 Packages

Next, the user will select which packages to be used.

1. Select the **Packages** button to open the *MT3D/RT3D Packages* dialog.
2. Turn on the following packages:
   - *Advection Package*
   - *Dispersion Package*
   - *Source/Sink Mixing Package*
3. Select the **OK** button.

6.5 Porosity Array

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

1. Select the **Porosity** button to open the *Porosity* dialog.
2. In the *Porosity* dialog, select **Constant → Grid** button to open the *Grid Value* dialog.
3. Enter "0.32."
4. Select **OK.**
5. Select **OK t**o exit the *Porosity* dialog.

This completes the definition of the Basic Transport package data. The user can leave the other options at the default values.

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

6.6 Run Options

Next, the user will tell MT3DMS to always use the same MODFLOW solution to define the flow field. This will allow the user to save the transport simulation under a different name without having to re-run MODFLOW.

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1. Select the *PHT3D* | **Run Options** command.
2. Select the *Single run with selected MODFLOW solution* option.
3. Select the **OK** button.

7 Advection Package

The Advection Package has been included in the simulation. The user will use the default settings in the package, so nothing needs to be edited in the Advection package.

8 Dispersion Package

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

1. Select the *PHT3D* | **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 "0.0067."
5. Select the **OK** button.
6. Select the **OK** button to exit the *Longitudinal Dispersivity* dialog.
7. Select the **OK** button to exit the *Dispersion Package* dialog.

9 Adding Inflow Concentrations

The flow model has been set up with a constant head of 12 ft on the left of the model and a constant head of 10 ft on the right. The flow should move from left to right through the model grid. For the first stress period, the user will only want the contaminated water going into 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.

9.1 Assigning Inflow Concentrations from Flushing Water

1. Choose the **Select Cells** tool.

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2. Select the 7 lower-most cells at in the leftmost column.
3. Right-click on one of the cells.
4. Select **Properties** command to open the *3D Grid Cell Properties* dialog.

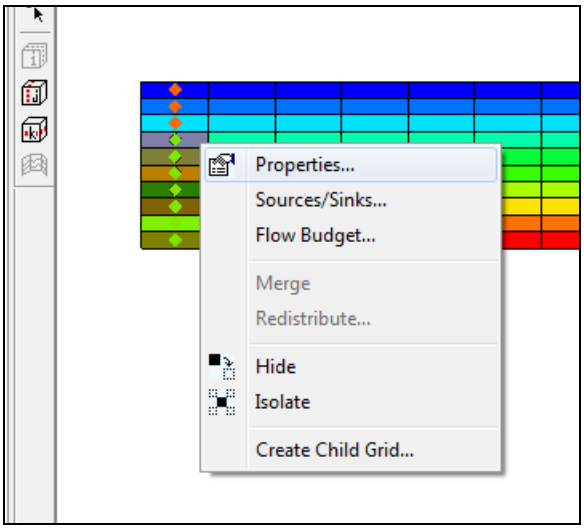

Figure 1 Assigning the constant concentration boundary condition

5. Select the *PHT3D* tab.
6. Change the ICBUND value to "-1."
7. Select the **OK** button to exit the dialog.

9.2 Assigning Inflow Concentrations from Contaminated Water

The user will now assign the inflow concentrations of the contaminated water.

1. Choose the **Select Cells** tool.
2. Right-click on the 3 upper-most cells in the leftmost column.
3. Select the **Sources/Sinks** command to open the *MODFLOW/PHT3D Sources/Sinks* dialog.

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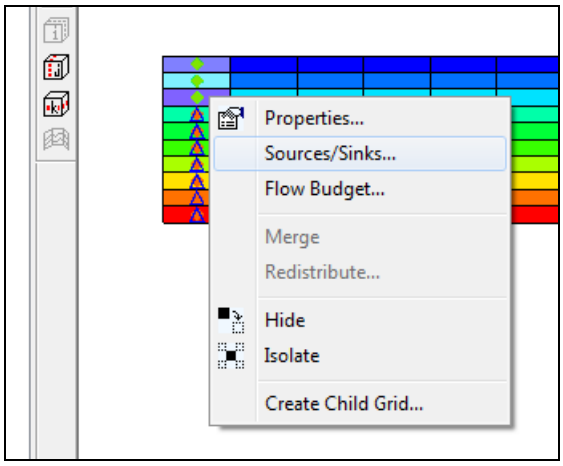

Figure 2 Assigning the contaminant concentration boundary condition

4. In the left window, select *PHT3D: Point SS* item.

5. Select the **Add BC** button.

The user can define the concentration in this dialog. However, the user will only want to assign the inflow concentrations of the contaminated water for the first stress period. It's easier to do this using the *Source/Sink Mixing Package* dialog.

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

7. Select the *PHT3D* | **Source/Sink Mixing Package** command.

In the *Point sources/sinks* section of the dialog, the user should see the 3 new boundary conditions listed in the spreadsheet.

8. By default, the stress period number should be 1.

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

10. Change the stress period to "2."

11. Enter the flushing water concentration, listed in Table 1, for each species in all three rows.

12. Click the **OK** button to exit the dialog.

Table 3 Aqueous component concentrations in contaminated water

Aqueous	**Contaminated water C_{cont} (mol/l)**
Amm	6.87×10^{-3}
O(0)	0
Ca	1.5×10^{-4}
Mg	5.0×10^{-5}

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Na	1.30×10^{-3}
K	1.30×10^{-4}
Cl	3.23×10^{-3}
C(4)	2.92×10^{-3}
C(-4)	0
S(6)	1.56×10^{-3}
N(5)	0
N(3)	0
N(0)	0
pH	8.3
pe	0

10 Saving the Simulation and Running PHT3D

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

1. Select the **Save** button.
2. Select the *MODFLOW* | **Run MODFLOW** command.
3. Select **Close** when the simulation finishes.
4. Select the *PHT3D* | **Run PHT3D** command.
5. When the simulation is finished, click the **Close** button.

11 Viewing the Solution

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

1. If necessary, expand the "pht3d_run1 (PHT3D)" folder from the Project Explorer.
2. Select the "Amm" dataset.
3. Click on the first time step in the *Time Steps* window below the Project Explorer.
4. Use the up and down arrows to view the different time steps.

The Ammonium is flushed out of the system.

11.1 Time Series Data Plot

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

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1. Select the "N(5)" dataset.
2. Select the **Plot Wizard** button.
3. Select the *Active Dataset Time Series* plot.
4. Select the **Finish** button.
5. Choose the **Select Cells** tool.
6. Select a cell in one of the top 3 layers near the middle of the model.

The user should be able to see the concentration of *N(5)* over time. The user may want to select different species from the Project Explorer to see how the concentrations vary with time.

7. When finished, close the plot window.

12 Ion Exchange Reactions

So far in this model, 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.

12.1 Define Exchange Species

1. Select the *PHT3D* | **Basic Transport Package** command.
2. Select the **Define Species** button.
3. Select the *Exchange Species* option in the left window.
4. Turn off the *Only show active species* check box.
5. Turn on the *Active* check box in the right window for *NaX, KX, AmmHX, CaX2,* and *MgX2*.
6. Select the **OK** button.

12.2 Define Exchange Species Initial Concentrations

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

1. In the spreadsheet, select the *CaX2 Species*.
2. Enter a value of "0.03363" for the starting Concentration.

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Use the same procedures described above to specify the initial concentrations for all the exchange species listed in Table 4.

3. Click **OK.**

Table 4 Exchange Species

Exchange Species	Concentration C_{init} (mol/l)
KX	2.66×10^{-6}
AmmHX	0
NaX	6.276×10^{-6}
MgX2	2.637×10^{-2}

13 Saving the Simulation and Running PHT3D

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

1. Select the *File* | **Save As** command.
2. Change the file name to "pht3d_run2.gpr."
3. Select the **Save** button.
4. Select the *PHT3D* | **Run PHT3D** command.
5. When the simulation is finished, click the **Close** button.

14 Viewing the Solution

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

1. If necessary, expand the "pht3d_run2 (PHT3D)" folder from the Project Explorer.
2. Select the "AmmHX" dataset.
3. Click on the first time step in the *Time Steps* window below the Project Explorer.
4. Use the up and down arrows to view the different time steps.

The user may want to select different exchange species from the Project Explorer to see how the concentrations vary with time.

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15 Conclusion

This concludes the "PHT3D – Ion Exchange and Surface Complexation" tutorial. Here are the key concepts 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.

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