PHT3D Tutorial

About PHT3D

PHT3D is a multi-component transport model for three-dimensional reactive transport in saturated porous media. The current version of Visual MODFLOW incorporates PHT3D v.1.46, which couples the two existing and widely used computer programs, the solute transport model MT3DMS (v5.1, Zheng and Wang, 1998) and the USGS geochemical code PHREEQC-2 (v2.9, Parkhurst and Appelo, 1999). The coupled model forms a powerful and comprehensive three-dimensional reactive multi-component transport model (Prommer et al., 2003), which can handle a broad range of equilibrium and kinetically controlled biogeochemical processes, including

- aqueous complexation
- redox reactions
- mineral precipitation/dissolution and
- ion exchange reactions.

Owing to the flexibility of PHREEQC, reaction networks can be defined quickly within a reaction database file. Reactive processes that are not included in the original PHREEQC database file can be appended, for example to simulate

- growth and decay of one or more bacterial groups
- dissolution from a multi-component NAPL (non-aqueous phase liquid) mixture

This allows PHT3D to act as a modeling toolbox that can be efficiently used to develop, adapt and apply site-specific and contaminant-specific reactive transport models. PHT3D uses the original PHREEQC database files and format for the definition of the geochemical reactions. Therefore it is possible to append, modify or exchange reaction databases, depending on the modeling task. Within Visual MODFLOW reaction networks are defined through the creation of reaction modules.

During its development PHT3D was applied to simulate the geochemical evolution within aquifers as well as their remediation. This included cases in which the natural and enhanced attenuation/remediation of organic contaminants was assessed, but also cases where the fate of inorganic pollutants is studied.

Sample Applications

Previous modeling studies using PHT3D were, for example, carried out to study

- the biogeochemistry of landfill leachate plumes
- aromatic and chlorinated hydrocarbon spills
- the fate of pesticides and the resulting isotopic fractionation
- trace metal remediation by in-situ reactive zones

- the fate of an ammoniacal liquor contamination
- an emplaced creosote source experiment
- the isotopic fractionation during natural attenuation of chlorinated ethenes
- the geochemical evolution under islands in the Okavango Delta, Botswana
- biogeochemical changes during ASR (aquifer storage and recovery) of reclaimed water
- temperature-dependent pyrite oxidation during a deep-well injection experiment
- the fate of a pharmaceutical residue during artificial recharge of groundwater
- remediation of acid mine drainage by permeable reactive barriers
- the reactive transport of chlorinated solvents in a permeable Fe(0)-filled reactive barriers
- the role of transverse dispersion on reactive contaminant transport
- the geochemical evolution of the capture zone of drinking water supply wells.

Geochemical Transport Modeling Problem

This tutorial illustrates PH3TD's application for a geochemical transport modeling problem where pyrite is oxidized during the injection of aerobic surface water. This exercise is a simplified, scaled-down version of the modelling study reported by Prommer and Stuyfzand (2005).

Background

Managed aquifer recharge is increasingly used to enhance the sustainable development of water supplies. Common recharge techniques include aquifer storage and recovery (ASR), infiltration ponds, river bank filtration (RBF) and deep-well injection. Following recharge the water quality of the injectant is typically altered by a multitude of geochemical processes during subsurface passage and storage. Relevant geochemical processes that affect the major ion chemistry include microbially mediated redox reactions, mineral dissolution/precipitation, sorption, and ion-exchange. The hydrochemical changes that occur under these circumstances, in particular the temporal and spatial changes of pH and redox conditions, are in many cases the controlling factor for the fate of micropollutants such as herbicides and pharmaceuticals. Similarly, changes in mineralogical composition such as dissolution and precipitation of iron- or aluminium oxides may affect the mobility of trace metals as well as the attachment and subsequent decay of pathogenic viruses. Laboratory and field-scale experimental studies are aimed at investigating such processes under controlled conditions and to eventually develop a better qualitative and quantitative understanding of their complex interactions, both site-specific and at a fundamental level.

Prommer and Stuyfzand (2005} carried out a reactive transport modelling study to analyze the data collected during a deep well injection experiment in an anaerobic, pyritic aquifer near Someren in Southern Netherlands.

This exercise replicates some of the key processes that were identified to influence water quality changes during subsurface passage. Pyrite oxidation will be defined as a kinetic process in which the reaction rate depends on the water temperature. For simplicity we include temperature as a separate aqueous (mobile) component. (Note, that by doing this, the heat transport problem is only approximated, and not solved exactly). The reaction rate expression has been programmed such that the value of the component representing the groundwater temperature is read and used during the computation of the reaction rate.

For more details, please refer to Prommer and Stuyfzand, (2005).

Requirements

NOTE: Some features described in this tutorial are only available in the Pro or Premium version.

The tutorial also assumes that the user has some understanding of MT3DMS, PHREEQC-2, and at least a basic understanding of geochemical processes and concepts.

Terms and Notations

For the purposes of this tutorial, the following terms and notations will be used:

Type: - type in the given word or value

Select: - click the left mouse button where indicated

⇔   - press the **<Tab>** key

↵   - press the **<Enter>** key

☞   - click the left mouse button where indicated

☞☞ - double-click the left mouse button where indicated

The **bold faced type** indicates menu or window items to click on or values to type in.

[...] - denotes a button to click on, either in a window, or in the side or bottom menu bars.

Opening the Visual MODFLOW Model

Getting Started

On your Windows desktop, you will see an icon for Visual MODFLOW.

☞☞ 🎲 Visual MODFLOW to start the program

The flow model underlying the geochemical transport problem treated in Example5 has already been built for you; to open this model,

☞ **File / Open** from the top menu bar.

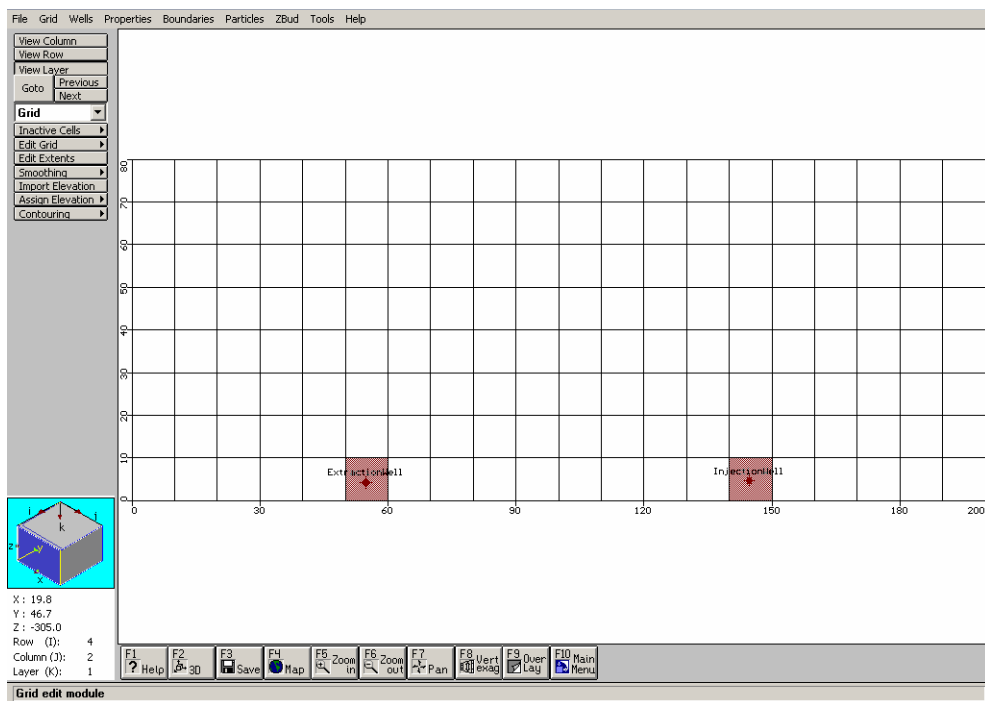Browse to the *C:\My Documents\Visual MODFLOW\Tutorial\PHT3D\Example5* folder, and locate the EX5.VMF file.

Select this file, and

☞ **[Open]**

This will load the input window of Visual MODFLOW; you will now briefly examine the input for this model.

☞ **Input** from the top menu bar

This will load the input window of Visual MODFLOW.

The model domain is 8 rows by 20 columns, and there is only a single layer. The X extent is 200m; Y extent is 80m.

We will now briefly review the inputs for this model.

☞ **Wells / Pumping Wells** from the top menu bar, to see the well data.

The study area has 2 wells, an extraction well pumping out the brackish water and an injection well pumping in fresh water.

☞ **Edit Well** from the side menu bar, then click on a well to view the well data.

The initial rate of the extraction well is -500 m³/day and the initial rate of the injection well is +500 m³/day.

☞ **Properties / Conductivity** from the top menu bar, click **No** when prompted to save changes.

☞ **Database** from the side menu to see the conductivity zones for the model. The default conductivity for this model is 10 m/day, and 10 m/day vertical conductivity.

☞ **Boundaries / Constant Head** from the top menu bar, click **No** when prompted to save changes. You can see that the model has a Constant Head of 20m defined at both the western and eastern extents of the model.

Next we will define the PHT3D reaction module for this model.

☞ **File / Main Menu** from the top menu bar, click **No** when prompted to save changes.

Define Reaction Module

The next step will be to define the reaction network (reaction module) and define the initial concentrations of aqueous (mobile) components and pyrite as well as the injectant concentrations.

Note: If you wish to skip this step, you may view the Visual MODFLOW solution files (completed project files with output), by opening the Ex5.vmf project from the directory: "Tutorial\PHT3D\Example5\solution_files\", and proceed to "View Output" on page 25 below.

Using AquaChem to Prepare PHT3D Input Data

This section demonstrates the convenience of using Waterloo Hydrogeologic's AquaChem software package to prepare the PHT3D input data for the Visual MODFLOW PHT3D Transport variant.

Note: The following steps require you to have AquaChem v.5.1 or greater installed on your machine. If you would like to skip this section, please proceed to "Add New Variant" on page 14 below; (the files generated from AquaChem are provided with the PHT3D Tutorial). To obtain a demo or trial license of AquaChem, please continue reading.

About AquaChem

AquaChem is a software package specifically tailored for anyone working with water quality data, and is ideally suited for water projects requiring management, analysis, and reporting of their water quality data. AquaChem features a fully customizable database of physical and chemical parameters and provides a comprehensive selection of analysis, calculation, modeling, and graphing tools. There is no other program on the market that offers all the features found with AquaChem!

AquaChem's analysis tools cover a wide range of functions and calculations frequently used for analyzing, interpreting and comparing water quality data. These tools include simple unit transformations, charge balances, statistics and sample mixing to more complex functions such as correlation matrices and geothermometer calculations. These powerful analytical capabilities are complemented by a comprehensive selection of commonly used plotting techniques to represent the chemical characteristics of aqueous geochemical and water quality data. The plot types available in AquaChem include:

- Correlation Plots: X-Y Scatter, Ludwig-Langelier, and Wilcox
- Summary Plots: Box and Whisker, Frequency Histogram, and Schoeller
- Multi Parameter Plots: Piper, Durov, Ternary, and Schoeller
- Time-Series plot (multi-parameter, multi stations)
- Geothermometer & Giggenbach Plots
- Single Sample Plots: Radial, Stiff, and Pie
- Thematic Map Plots: Bubble, Pie, Radial and Stiff plots at sample locations

Each of these plots provides a unique interpretation of the many complex interactions between the groundwater and aquifer materials.

Generate PHT3D Input Data

For in-depth geochemical modeling, AquaChem features a built-in link to the popular geochemical modeling program PHREEQC for calculating equilibrium concentrations (or activities) of chemical species in solution and saturation indices of solid phases in equilibrium with a solution. Using AquaChem v.5.1, you can also produce PHT3D input files for use with in Visual MODFLOW v.4.2 or higher.

In the current version, Visual MODFLOW data entry for PHT3D is based on the same user interface that facilitates data input for other transport engines such as MT3DMS and RT3D.

In contrast to typical model applications of the former transport engines, your PHT3D model will be comprised of many more species (components), which can lead to a

PHT3D Tutorial

much more tedious data input. Furthermore, PHT3D only accepts molar-based concentrations and the aqueous solutions that define water compositions need to fulfill special conditions such as being perfectly charge-balanced, different redox-states of elements must be defined separately, total inorganic carbon concentrations must be entered instead of alkalinity, etc.

Therefore analytical results from the laboratory normally need to be pre-processed before the data can be entered in PHT3D. To facilitate an efficient workflow, Visual MODFLOW includes an import feature, which allows the user to conveniently import solutions, minerals and ion exchanger compositions into a selected set of cells. AquaChem, in turn, allows for export of the information stored in its database into the format that can be imported into Visual MODFLOW.

Typically setting up a PHT3D model is comprised of the following major steps:

- definition of the initial composition of the aqueous solution (groundwater), i.e., aqueous concentrations of all components
- entry of matrix (aquifer) properties: mineralogical composition and initial
- ion exchanger composition
- definition of the water quality at model boundaries (sources): solution composition of, for example, in-flowing, infiltrating, recharged or injected water

The operations described below are required to transform laboratory results into PHT3D ready input for the Visual MODFLOW project.

Open AquaChem Project

Before proceeding, minimize the Visual MODFLOW window.

To start AquaChem, click **Start** and choose **Programs/Waterloo Hydrogeologic/Aquachem/Aquachem**, or double-click on the desktop icon.

When AquaChem starts, it displays an **Open Database** dialogue prompting you to select an AquaChem database to open.

☞ Browse to your Visual MODFLOW installation\Tutorials directory, and locate **AquaChem_PHT3D_Demo.AQC** in the PHT3D\Example5 directory (default is C:\My Documents\Visual MODFLOW\Tutorial\PHT3D\Example5).

☞ **[Open]**

The Demo database file should then be loaded into AquaChem, and the following window should appear.
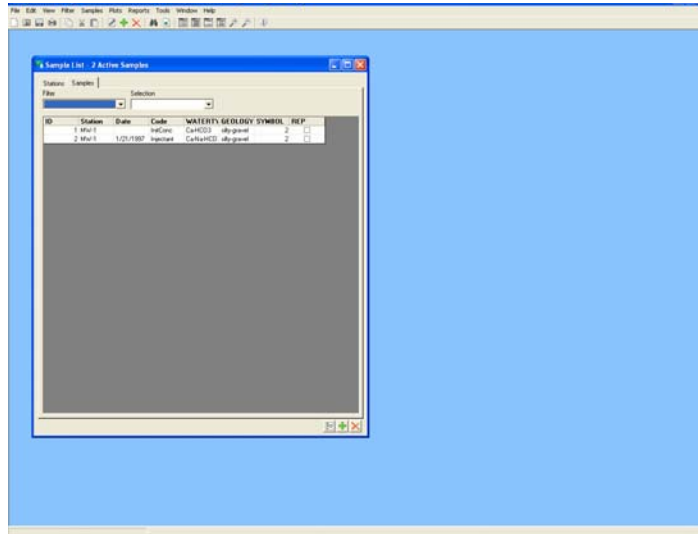
Note: You may need to adjust the size of this window in order to see all the rows and columns in the database table.

Note: The features and usability of AquaChem is outside the scope of this tutorial; if you are a new user to AquaChem, please refer to the Getting Started section in the AquaChem help, or the Demo Guide, to familiarize yourself with this software.

Define Output File Settings

To create a PHT3D input file:

☞ **Generate PHT3D Input** from the **Tools > Modeling** menu, and the screen depicted in figure below will appear.
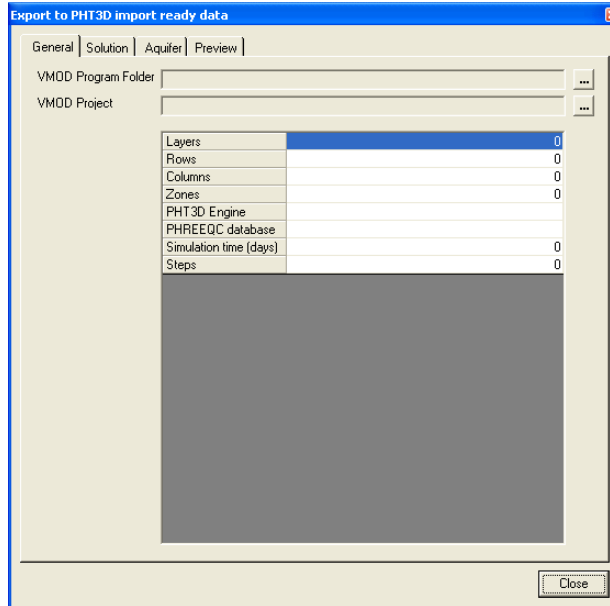
The **VMOD Program Folder** field allows the user to select the VMOD installation folder (by default the folder is C:\Program Files\Visual MODFLOW). This folder contains the VMOD.xml file which is required to locate the PHREEQC thermodynamic database.

      ☞ [...] button in the top right corner

      ☞ Locate the VMOD installation folder (default is C:\vmodnt)

      ☞ **[Ok]**

The **VMOD Project** field allows the user to specify the VMOD project file (*.vmf) which contains general information about the project's layers, rows, columns, simulation duration and species.

      ☞ [...] button in the top right corner

      ☞ Browse to your Visual MODFLOW installation\Tutorial directory, and locate **PHT3D\Example5** directory (default is C:\My Documents\Visual MODFLOW\Tutorial\PHT3D\Example5)

      ☞ **Ex5.vmf**

      ☞ **[Open]**

      ☞ **Solutions** tab

Solutions Tab

All units must be expressed in mol/l, plus there must be a perfect charge balance between anions and cations. This is achieved by first running a PHREEQC simulation and allowing an automatic charge adjustment, typically on an element which is sufficiently abundant to achieve a balance and which is not considered important for the type of reactions studied through this model. In many cases chloride is a good candidate. Further, PHT3D requires total inorganic carbon as input as opposed to alkalinity which is usually reported in lab results. Again, this requires that the original solution is run and total inorganic carbon is read back from the simulation output file.

Now you will need to choose the samples to be included in the PHT3D input file.

) Click the **[Select]** button to open the **Samples** window. The following window will appear.
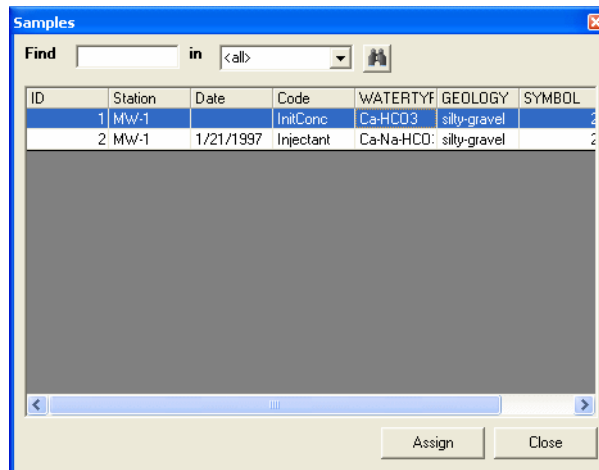
)) Double click on a sample ID=1 (InitConc) to add it to the PHT3D Input file.

All available concentrations in the selected sample will be copied in the "Conc" column in their original format.

Next, select the element to be used for balancing cations and anions from the **Charge Balance** combobox.

) **Cl** from the **Charge Balance** combobox

Upon selecting, the PHREEQC simulation will launch automatically and update the mols/L column with the results.
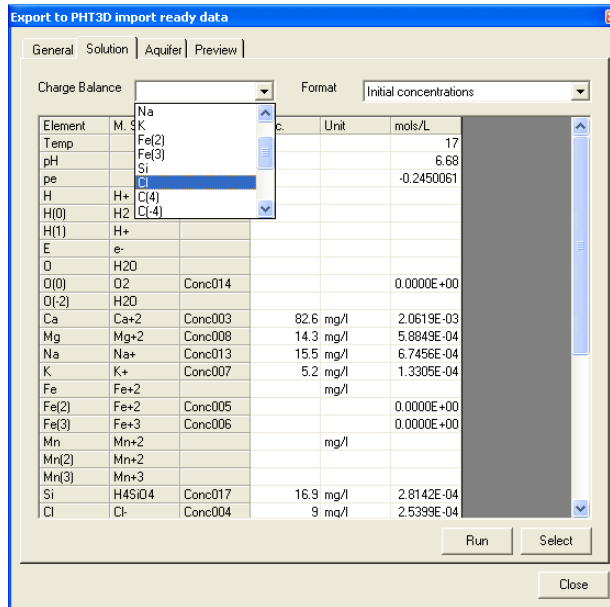
☞ **Aquifer** tab

Aquifer Tab

The Aquifer tab is divided into two parts: **Minerals** and **Exchangers**.

Minerals

Typically, the laboratory results are provided in ppm or percentage mineral related to 1 kg of aquifer material. PHT3D requires the number of mols of mineral contained in one liter of bulk volume (=pore water + aquifer matrix). This requires knowledge about the porosity and density of the aquifer material. For example, an aquifer having porosity of 20% and density of 2.7 g/cm^3 will have a volume of 4 liter of rock around every liter of pore water resulting in a mass of 10.8 kg of rock material. If this rock comprises 10% of calcite, the mols of calcite is calculated as 10.8 * 0.1 * FMW(calcite, 0.1 kg) 10.08 mols. This calculation needs to be repeated for each mineral.

In this example, the Pyrite value has already been provided in mol/l, therefore it is not necessary for you to run additional calculators. However, you may experiment with these settings, by clicking on the ▦ button. When you are finished, return to the Aquifer tab.

☞ **mols/L bulk material** column, and type = 0.01

The screen should now appear as shown below.
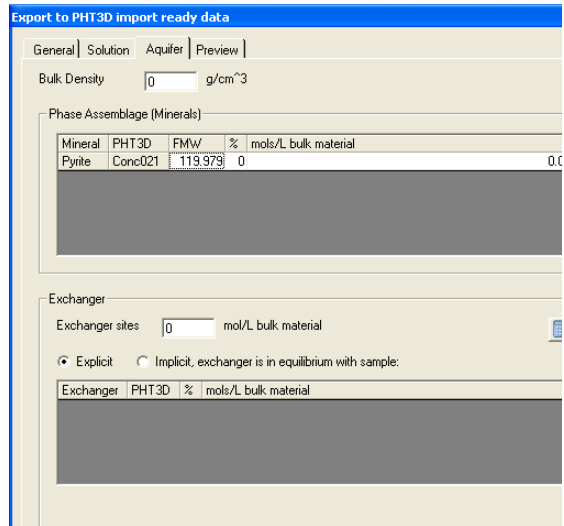
Exchangers

For this reaction module, Exchangers are not required; however some brief information on how these are prepared in AquaChem is described below.

PHT3D requires the amount of exchange places and the initial occupation of these places with various available ions, e.g. NaX, CaX2, MgX2, KX, etc. As in the previous case, the concentrations refer to 1 liter of pore water, though in reality, these values are rarely available. Values provided by the laboratory normally include the CEC (cation exchange capacity, which may be transformed into exchange sites per liter of pore water in a similar way as discussed for the minerals. More often, the CEC itself has to be estimated based on the amount and type of clay minerals and presence of organic material. A formula that is often applied in this respect is given by Appelo and Postma, 2005:

CEC = 3.7 * %clay + 3.5 * % organic C

If the type of the dominant clay material is known, then the CEC can also be estimated by multiplying the average CEC of this clay material with the percentage reported in the studied aquifer material.

All above methods only provide the total number of sites available for ion exchange, but do not indicate the initial occupation of these places. If an exchanger material assumed to be in equilibrium with a given aqueous, then PHREEQC allows calculating this initial composition using the so-called implicit option for the exchange simulation. As for the solution, the PHREEQC output can then be used as input for PHT3D.

We will now preview and export the solution and mineral data to text files, which can then be imported into VMOD.

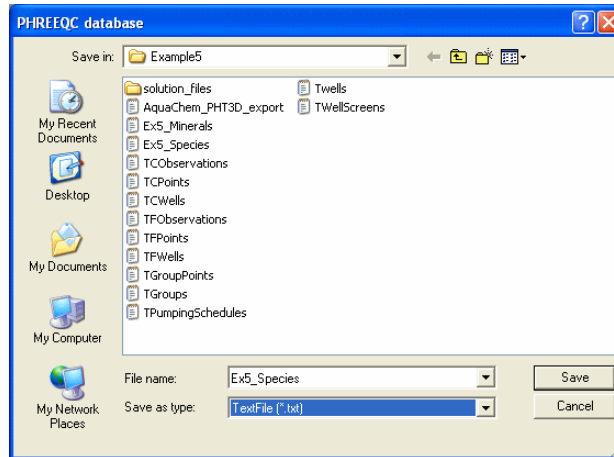☞ **Preview** tab

Preview

The **Preview Tab** allows you to preview the prepared solution, minerals and exchanger data before exporting to text files.
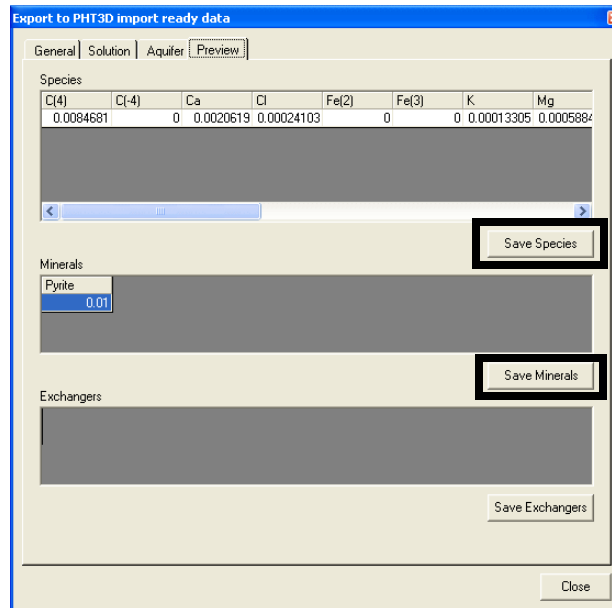
Exporting

First we will export the solution values. To do so,

☞ **Save Species** button

Leave the default **File name** (Ex5_Species) and **Location** (C:\My Documents\Visual MODFLOW\Tutorial\PHT3D\Example5).

☞ **[Save]** button.

Next, export the mineral values,

☞ **[Save Minerals]** button

Leave the default **File name** and **Location**, and click the **[Save]** button.

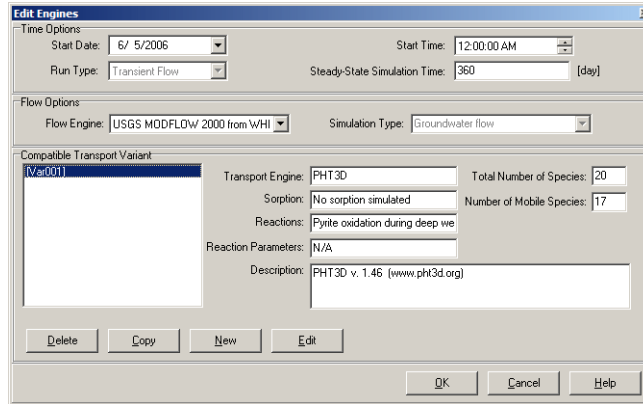These text files can now be imported into VMOD/PHT3D.

☞ **[OK]**

☞ **[Close]** in the Export to PHT3D window.

You may now close AquaChem, and activate Visual MODFLOW and continue with defining the Visual MODFLOW input.
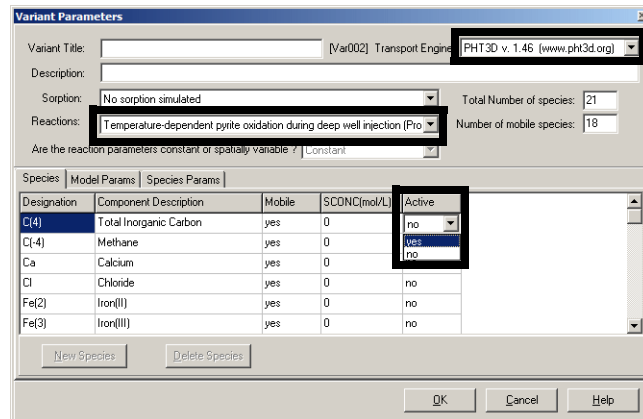
Add New Variant

☞ **Setup / Edit Engines** from the top menu bar

In the Edit Engines dialog,

- ☞ **[New]** button

- ☞ **PHT3D v.1.46** from the picklist in the upper right corner, then

- ☞ **Temperature dependent pyrite during deep well injection**

- ☞ **Yes** in the Active column for every species

These settings are highlighted in the image below:

After the reaction is selected, the list of components (species, minerals and exchangers) for this reaction will be populated in **Species** tab of the table below. The first step is to define the initial concentrations (SCONC) for the species and minerals which are present at the start of the simulation (ambient geochemical conditions). Note, these concentrations can be defined (now) through the input module or (later) in the grid. In this example, we will demonstrate how to define concentrations in the input module.

☞   **[OK]**

☞   **Var001** from the list of variants in the grid box

☞   **[OK]**

Once this is complete you will enter injectant concentrations.

Define Initial Concentrations

☞   **Input** from the main menu bar

☞   **Properties / Initial Concentration** from the main menu bar

The intial concentrations for this reaction are presented in the table below.

Table 1: Initial Concentrations

Mineral	Initial Concentration (mol/l)
C(4)	0.00845
C(-4)	0
Ca	0.00206
Cl	0.000254
Fe(2)	0.000104
Fe(3)	1.34E-12
K	0.000134
Mg	0.000588
N(5)	0
N(3)	0
N(0)	0
Amm	0
Na	0.000675
O(0)	0
S(-2)	0

Mineral	Initial Concentration (mol/l)
S(6)	5.52 E-5
Si	0.000281
Tmp*	0.017
pH	6.68
pe	-2.45
Pyrite	0.01

*Tmp 0.017 corresponds to 1/1000 of the temperature in Celsius (=17 C).

Enter the SCONC (Initial concentrations) according to the values listed in the table above. In Visual MODFLOW, there are two options for defining concentrations:

- Define Manually, one-at-a-time for each species;
- Import from Text File, which can be generated using AquaChem; this option is only available if you completed the section "Using AquaChem to Prepare PHT3D Input Data" on page 5 above.

Please select the appropriate option below.

Define Manually

☞ **[Database]** button from the side toolbar

Enter the initial concentration for the first species, C (4) for zone 1. Enter the value of 0.00845.

☞ **[OK]**

☞ **[C(-4)]** from the species combo box on the side toolbar

Repeat the steps above to define the concentration for this species. Continue these steps for the remainder of the species listed in Table 1 above. When you are finished, proceed to "Defining Point Source Concentrations" on page 18 below.

Import from Text File

☞ *Right-mouse* click anywhere in the model domain

☞ **Import Species**

☞ Browse to your Visual MODFLOW installation directory, and locate **Example 5** directory (default is C:\My Documents\Visual MODFLOW\Tutorials\PHT3D\Example5)

☞ Ex5_Species.txt

☞　　**[Open]**

Repeat this for the Minerals

☞　　**Import Minerals**

☞　　Browse to your Visual MODFLOW installation directory, and locate
　　Example 5 directory (default is C:\My Documents\Visual
　　MODFLOW\Tutorials\PHT3D\Example5)

☞　　Ex5_Minerals.txt

☞　　**[Open]**

You may confirm that species were imported successfully by randomly selecting one
from the combo-box on the side toolbar, and comparing this to the concentration listed
in Table 1.

When you are finished, proceed to "Defining Point Source Concentrations" on page 18
below.

Defining Point Source Concentrations

☞　　**Boundaries / Point Source** from the top menu bar. Click **[Yes]** when
　　prompted to save changes.

In order to correctly represent the water flowing across the model, the water
composition at the left boundary should be the same as the initial concentrations.

☞　　**[Assign / Single]** from the side toolbar. The Assign Point Source dialogue
will appear. Move the mouse cursor over the cell in the top left corner (Row1, Col1,
Layer1), and click once. Repeat this for each cell in column 1, until you reach the lower
left corner (Row8, Col1, Layer1).

In the **Assign Point Source** dialog, enter the concentrations as per Table 1 above.

☞　　**[OK]** when you are finished.

The injectant concentrations will be assigned to the influent at the injection well. To
view the injection well, you must activate this overlay in the Overlay control:

☞　　**F9 (Overlay Control)** button from the toolbar at the bottom.

☞　　**BC(F) - Wells** to activate this overlay

☞　　**[OK]**

☞　　**[Assign / Single]** from the side toolbar. Move the mouse cursor over the
　　injection well (Row 8, Column 15), and click once. The following dialog will
　　appear:
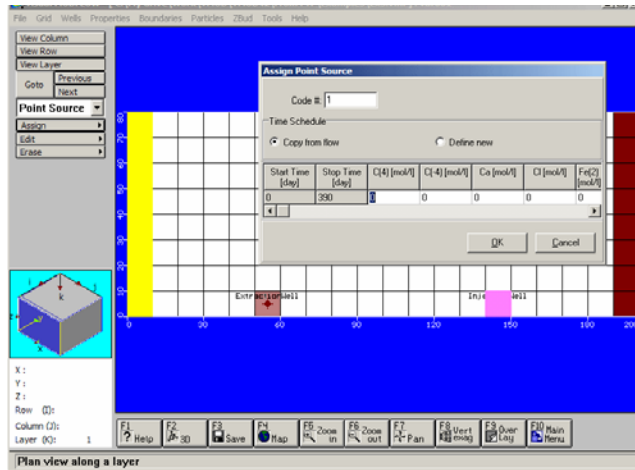
☞ **Define new** radio button

Enter the injectant concentrations as per Table 1 in Prommer and Stuyfzand 2005, as shown below:

Table 2: Point Source Concentrations

Mineral	Concentration (mol/l)
C(4)	0.00314
C(-4)	0
Ca	0.00187
Cl	0.00182
Fe(2)	0
Fe(3)	2.68 E-7
K	0.000123
Mg	0.000325
N(5)	0.000354
N(3)	0
N(0)	0
Amm	0
Na	0.00126

| Mineral	Concentration (mol/l)
O(0)	0.000813
S(-2)	0
S(6)	0.000490
Si	0.000303
Tmp*	0.0019
pH	N/A
pe**	N/A
Pyrite	N/A

*Tmp 0.0019 corresponds to 1/1000 of the temperature in Celsius (=1.9 C)

**pH and pe are properties of the aqueous solution and in principle these properties are transported. However, for PHT3D, these species are treated as immobile. pH is computed through a charge balance equation and pe by transporting different redox components separately.

- ☞ In the End Time cell of the first row (which should display 360)

- ☞ Alt+Ins on your keyboard 12 times. This will create a total of 12 stress periods. As inserting a stress period automatically halves the previous end time, you will need to specify the end times for the stress periods.

- ☞ In the End Time cell of the second last row (which should display 195)

  Type: 330 in the cell. Keep moving up and in each successive cell enter the number of days reduced by 30.

When you are finished, the dialogue should look as follows:
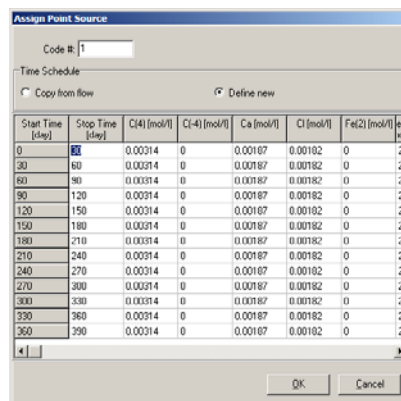
While the concentrations of the various chemicals remain constant, the temperature of the injected water is varying seasonally. Enter the following temperatures into their corresponding stress period:

Stress Period	Temperature
0-30	0.0019
30-60	0.004
60-90	0.01
90-120	0.013
120-150	0.017
150-180	0.02
180-210	0.024
210-240	0.022
240-270	0.018
270-300	0.012
300-330	0.008
330-360	0.004

☞   **[OK]**

You are now ready to review the PHT3D Run settings, and then run the MODFLOW + PHT3D simulation.

Run PHT3D Simulation

☞   **File / Main Menu** from the main menu bar

☞   **Run** from the main menu bar

MODFLOW Time Steps

The first step is to define the MODFLOW Time Steps

☞   **MODFLOW 2000 / Time Steps** from the main menu bar

The frequency of the PHREEQC reaction steps is controlled by the number of MODFLOW time steps. The accuracy of the results will depend on the number of time steps. Therefore, you will now define the time-stepping for MODFLOW 2000.
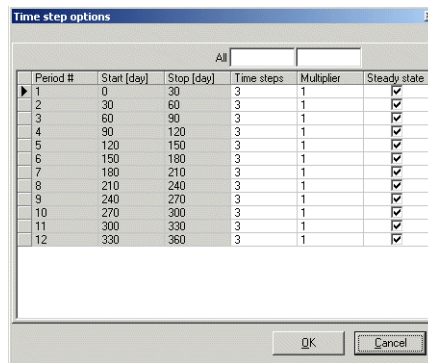
For each stress period of 30 days there should be 3 time steps. This means that the step length for the PHREEQC reaction steps are 10 days.

type: 3 for the **Time Steps**

type: 1 for the **Multiplier**

☞ **Steady-State** check box

Repeat this for each stress period; when you are finished, the Time Steps dialog should be similar to the one shown below.

Period #	Start [day]	Stop [day]	Time steps	Multiplier	Steady state
1	0	30	3	1	☑
2	30	60	3	1	☑
3	60	90	3	1	☑
4	90	120	3	1	☑
5	120	150	3	1	☑
6	150	180	3	1	☑
7	180	210	3	1	☑
8	210	240	3	1	☑
9	240	270	3	1	☑
10	270	300	3	1	☑
11	300	330	3	1	☑
12	330	360	3	1	☑

☞ **[OK]**

PHT3D Output Time Steps

The next step is to define output time steps for PHT3D.

☞ **PHT3D / Output/Time Steps** from the main menu bar

Confirm that the Simulation Length is 360 days. If not, enter this now.

Activate the option "Save Simulation Results at Specified Time (Days), and add the following output time steps:

30
60
90
120
150
180
210
240

PHT3D Tutorial
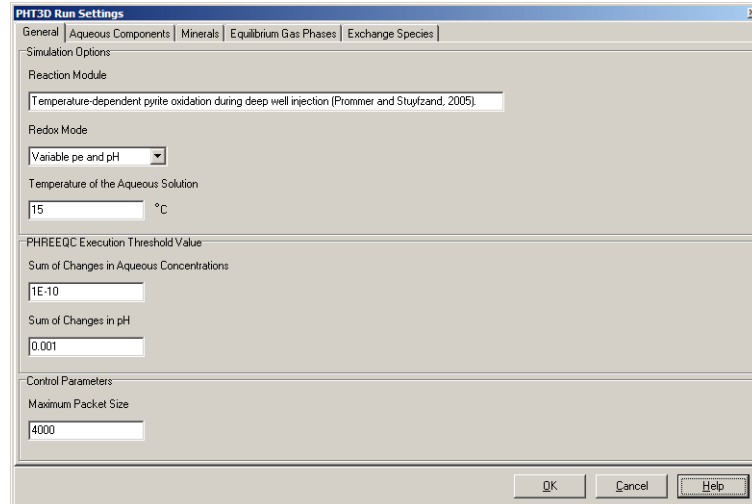
270
300
330
360

☞   **[OK]**

PHT3D Run Settings

In this section, you will review the PHT3D Run Settings. For this exercise, it is not necessary to modify the Run Settings.

☞   **PHT3D / PHT3D Run Settings** from the main menu bar, and the following dialog will appear:

The first tab, **General**, allows you to define the run settings. For this example, the default settings are acceptable. For more details, please consult the Visual MODFLOW Users Manual.

Some reaction modules require defining additional parameters for components, minerals, gases, etc. For this reaction module, there are parameters for Pyrite.

☞   **Minerals** tab

☞   **Kinetic** child tab
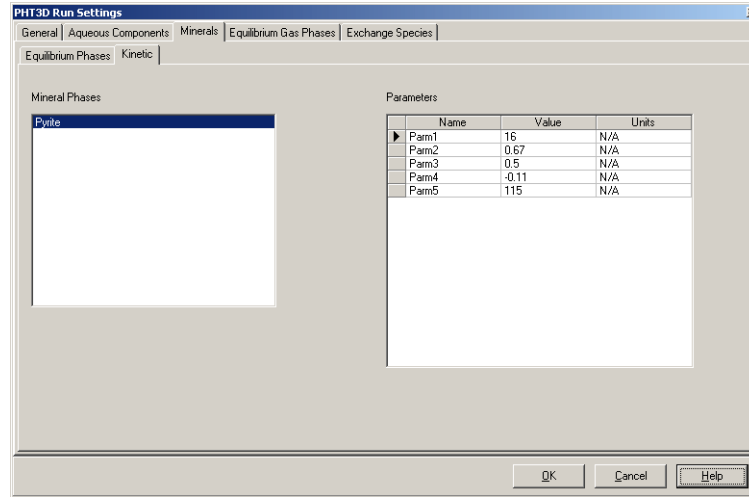
The parameter names originate from the PHREEQC Users Manual. In this example, it is not necessary to modify the default parameter values. For more details, please consult the Visual MODFLOW Users Manual.

> ☞ **[OK]**

Run MODFLOW 2000 & PHT3D

You are now ready to run the PHT3D + MODFLOW 2000 simulation

> ☞ **Run** from the main menu bar
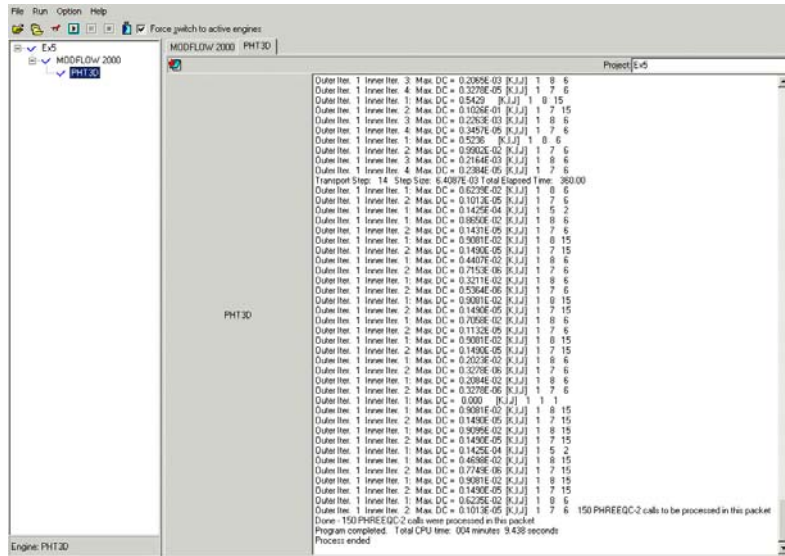
In the Engines to Run dialog,

> ☞ **MODFLOW 2000**
>
> ☞ **PHT3D**
>
> ☞ **Translate & Run**

The MODFLOW 2000 and PHT3D numeric engines will then run. This simulation length will vary, depending on system resources, buy may range from 60 seconds to 2-3 minutes.

The PHT3D simulation will be complete, when you see a blue check mark beside the PHT3D node in the engines tree, as shown below.

   ☞   **File / Exit** from the main menu bar of the VMEngines window, to close this window. You are new ready to view the output.

View Output

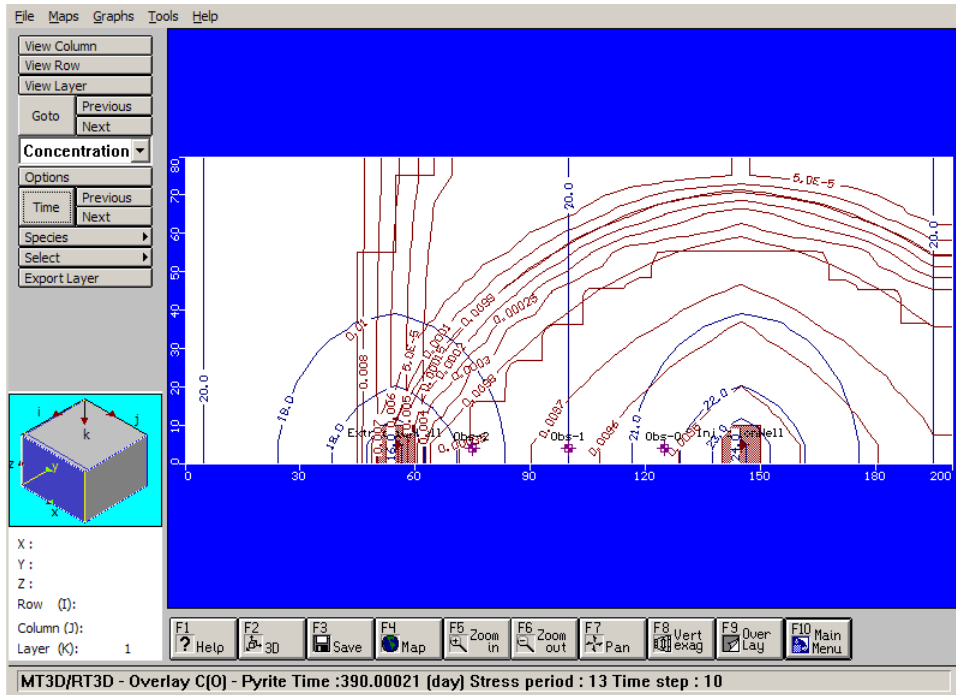To view the output,

   ☞   **Output** from the main menu bar.

Concentration Contours

To view the concentration contours,

   ☞   **Maps / Contouring / Concentration** from the main menu bar

   ☞   **Species** from the toolbar on the left side, and **Pyrite** from the species list

   ☞   **Time / Next** from the side toolbar, to advance through the time steps

The concentration results for Pyrite, after 360 days, are shown below.

MT3D/RT3D - Overlay C(O) - Pyrite Time :390.00021 (day) Stress period : 13 Time step : 10
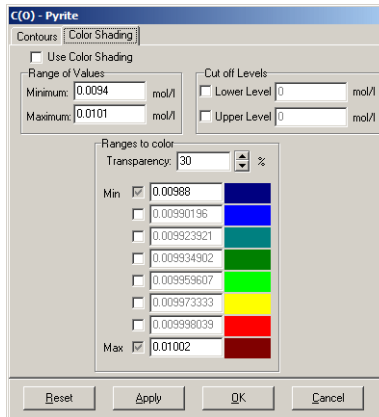
Repeat this for other species in the output.

To view the concentration contouring as a color map

    ☞   **Options** from the side toolbar, to advance through the time steps. The following dialogue will appear:
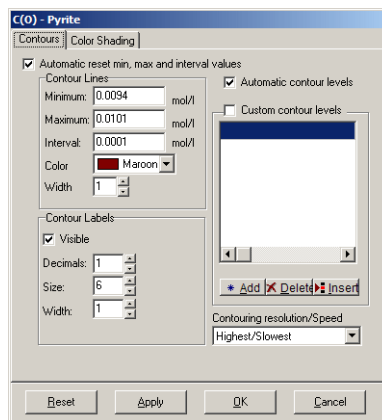
For better resolution, increase the number of **Decimals** in the **Contour labels** to 5.

    ☞   **Color Shading** tab to get the color map options:

> ☞ **Use Color Shading** check box. In this dialogue, the highest and lowest values for the selected parameter are automatically set as Max and Min, however you can change these values to create a cut-off.

> ☞ **[OK]** when you are finished and the color map of your results will be generated.

Besides the parameters you wish to view, there are several other contours displayed and they may be confusing the picture. To keep only the contours that you wish to examine, click **F9** on your keyboard and that will bring up the **Overlay Control** dialogue. In this dialogue you may wish to uncheck such overlays as Head Equipotentials as well as any parameters that you are not currently looking at, leaving only the one examined. In this case, make sure that out of the C(0) group, only the C(0) - Pyrite is checked. This way the contours you are looking at will not be confused with any others.

> ☞ **[Apply]** after unchecking any individual parameter to view what difference it makes on the map.

> ☞ **[OK]** when you are finished and the **Overlay Control** dialogue will close

Scroll through time using **[Previous]** and **[Next]** buttons beside the **[Time]** button on the side bar. You can see that pyrite concentrations decrease as a result of pyrite oxidation, with the lowest values being closest to the injection well where there is a continuous influx of oxygen.

Using the procedure described above, create a color contour map for O(0) species. Also scroll through the time to view the progression of oxygen in the aquifer. You can see as a large bubble forms initially, however it decreases due to the increase of the pyrite oxidation rates because of the higher temperature of the injection water.

Concentration Time Series Plots

It is also useful to see how the concentrations of certain parameters differ over time, using BreakThrough Curves (BTC's). 3 observation wells have been added to the model and you can generate time series graphs based on the generated results. To do so,

☞ **Graphs/Times Series/Concentration** from the top menu. In the window that appears,

☞ **Points** tab

☞ Check Obs_0/A, Obs_1/A, and Obs_2/A. These are the observation wells and you will be looking at the results from each of them.

☞ **Species** tab

☞ Uncheck C(4) and check O(0)

☞ **[Apply]**
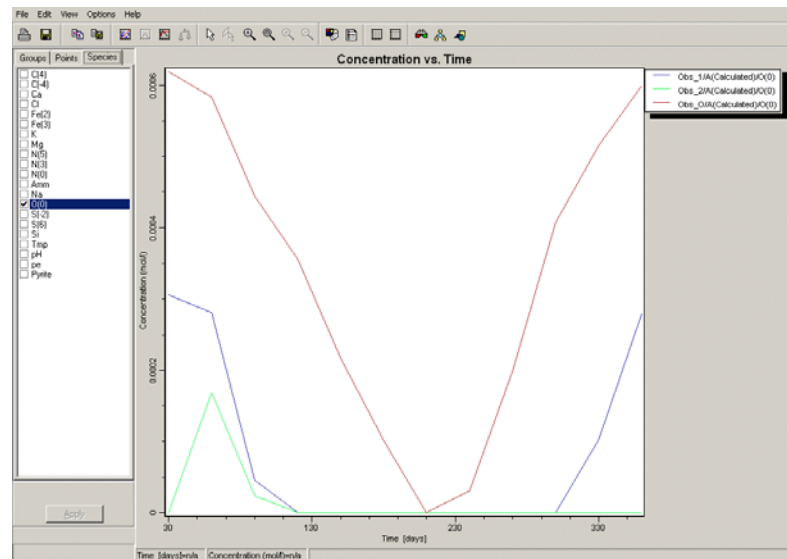
You can see the consumption of Oxygen along the flowpath and the seasonal variability resulting from the temperature variability.

Repeat the procedure and view the time series for S(6) and N(5) (sulfate and nitrate).

You can also view several parameters as observed at the same observation point.

☞ **Points** tab

☞ Deselect all observation wells except for Obs_1/A

☞ **Species** tab

☞ Select O(0), S(6), and N(5)

The following graph will appear:
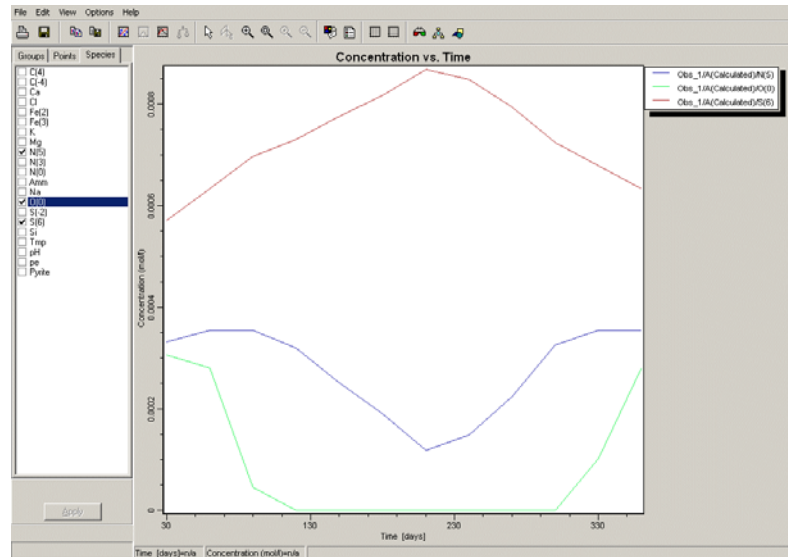
In this plot, you can observe the following effects:

- Nitrate concentrations remain constant and denitrification only starts when oxygen is fully depleted
- Both oxygen and nitrate are consumed by pyrite oxidation at seasonally changing rates, while sulfate is being produced. Therefore the sulfate concentrations at the observation points increase during the summer period, when the temperature of the injection water is higher.

This concludes the PHT3D tutorial, however feel free to explore other features this program has to offer using this and other provided examples.

Summary

The results of the simulation shows, that depending on the temperature of the injection water (all other parameters for flow & transport remain constant), the depth of oxygen penetration into the target aquifer is varying seasonally. Where oxygen is depleted denitrifcation starts to occur. The variability of the pyrite oxidation rates leads to variable sulfate concentrations, which increase along the flowpath as a result of pyrite oxidation.

References

Appelo, C.A.J. and Postma, D., 2005, 2nd ed: *Geochemistry Groundwater and Pollution*. A.A. Balkeema. Rotterdam, 634 p.

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Visual MODFLOW 2010.1 Users Manual

Prommer, H., and Stuyfzand, P.J. *Identification of Temperature-Dependent Water Quality Changes during a Deep Well Injection Experiment in a Pyritic Aquifer.* Environ. Sci. Technol. 2005, 39, 2200-2209

References