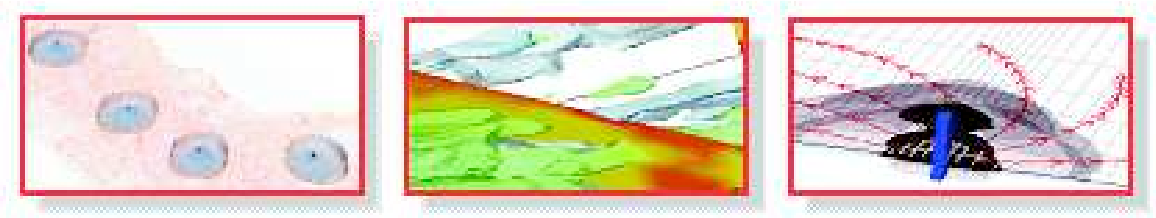
Short Course

Applied Reactive Transport Modelling

University of Bordeaux, France
24 – 28 March, 2014



Prepared by:
Henning Prommer (Henning.Prommer@csiro.au)
Vincent Post (vincent.post@flinders.edu.au)
Chunmiao Zheng (czheng@ua.edu)
James A. Davis (mrwaterx@gmail.com)
Olivier Atteia (olivier.atteia@ipb.fr)

Contents

Introduction

Knowledge of the chemistry of groundwater is a requirement for a number of practical purposes. As groundwater is an important source for drinking water, one has to ascertain that its quality is sufficient for consumption. Quality requirements are equally important for other types of utilization such as irrigation or industrial purposes, as well as for the protection of vulnerable ecosystems. More recently, pollution and clean up of aquifers has become a major topic in aqueous geochemistry. Furthermore, understanding of geochemical processes is needed for safety assessment studies, e.g. for the storage of nuclear waste.

Clearly, there are numerous practical applications for aqueous geochemistry. Moreover, geochemistry is an essential tool for understanding the hydrogeological systems that we study. It provides information on the provenance of groundwater, on flow directions and on groundwater ages.

Water quality patterns in aquifers can be complex. The input of different sources of water is the first of factors that adds to this complexity. Sources include precipitation, rivers, lakes (possibly polluted or saline due to strong evaporation), seawater, ascending deep groundwater and anthropogenic sources such as wastewater or irrigation return flow. Geochemical processes add to the complexity since they alter the waterŠs composition as it travels through the subsurface. Mineral dissolution and precipitation, ion exchange (transfer of solutes between solution and solid) and redox processes (reactions that involve electrons) are the 3 main categories of chemical processes that determine water quality. Mixing of different water types, which is more a physical than a chemical process, further exerts great influence on the composition of groundwater.

Figure 1 illustrates the chemical processes that influence the concentration of the major ions of groundwater as it flows from the recharge area towards the sea. Sulfate (SO_4^{2-}) derives from mineral sources such as pyrite and gypsum as well as from seawater and may be lost by conversion to HS^-, e.g. by oxidation of organic matter. Bicarbonate (HCO_3^-) is formed in the recharge area when CO_2 is produced by aerobic respiration and decay of organic matter in the soil zone. Its concentration is further influenced by mineral equilibria (e.g. calcite, dolomite, siderite) and redox reactions that involve sources of organic carbon in the aquifer itself. Sodium (Na^+) is contained in some silicate minerals that may dissolve but mainly originates

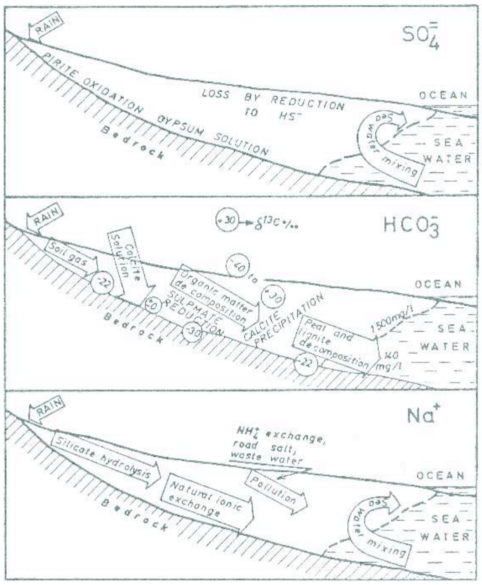


Figure 1: Schematic representation of chemical processes that influence the concentration of major ions in coastal areas (**?**).

from seawater. Cation exchange is the most important chemical process that affects its concentration. Calcite ($CaCO_3$) is abundant in many geological settings and constitutes the most important source for calcium (Ca^{2+}) in groundwater. Ca^{2+} also derives from other minerals such as dolomite, gypsum and feldspars and also takes part in cation exchange reactions. Magnesium (Mg^{2+}) finally, has a high concentration in seawater and is contained in some minerals, the most important being dolomite. Similar to Na^+ and Ca^{2+} it can be adsorbed to the exchange complex.

Considering the numerous sources and processes that influence solute concentrations, investigators that try and study the chemistry of aquifers are faced with an overwhelming complexity. Traditional methods that are applied to make sense of the vast pile of numbers that follow from the chemical analyses of water samples involve plotting (**?**) and classification of samples into groups (e.g. **?**) in order to be able to discern regional trends and to identify chemical processes. No matter how useful these methods are in deriving an idea of the reaction scheme that has given the water sample its composition, they are incapable of determining whether this scheme is feasible from a chemical point of view. In order to check whether a concept obeys basic chemical theory one needs a geochemical model that is based on the firm laws of thermodynamics. Or, as **?** put it: 'Quantitative models force the investigator to validate or invalidate ideas by putting real numbers into an often vague hypothesis and thereby starting the thought process along a path that may result in acceptance, rejection, or modification of the original hypothesis'.

Geochemical models were originally developed in the 1960's to calculate the speciation dissolved ions. The original models were soon improved and extended to include chemical reactions that alter the water composition such as mineral equilibria and cation exchange (**?**). By virtue of the increase in computer computational power it became possible to couple geochemical models with hydrological models to calculate how the water composition changes as it travels through the subsurface (**?**). Today's models have reached a level of sophistication that allows us to simulate real-world processes to understand and explain field observations (**?**).

Elaborate treatment of the basic concepts and applications of aqueous geochemical modeling can be found in for example **?** and **?**. This course manual provides a treatment of the basic principles of the models as well as exercises for MT3DMS (**?**), PHREEQC-2 (**?**) and PHT3D (**?**). Extensive use is made of the following packages:

- PHREEQC for Windows, a graphical user interface for PHREEQC which has the advantage that it's not necessary to switch between programs to create input, perform calculations or view output. The program can be installed on any computer that has Windows95 or higher. It can be obtained for free from:

  http://pfw.antipodes.nl/download.html
- PMWIN (8.15), a graphical user interface for MODFLOW, MT3DMS, SEAWAT and PHT3D. For information on how to order a fully functional copy of the software contact the author of the program, Wen-Hsing Chiang (wchiang@pmwin.net) or see http://www.simcore.com

Course outline

Many students and researchers that are introduced to reactive transport modelling for the first time are overwhelmed by the apparent complexity of it. Mastering the subject requires not only understanding of the underlying theory of groundwater flow, solute transport and hydrochemistry, but also of the many options that the modelling software packages offer. It often takes quite some time before students are confident enough to build and apply their own models. Although reactive transport modelling can indeed be complex, one should not be scared away from it as mastering this subject provides powerful applications. Even the simplest calculations of equilibrium speciation and saturation states already add to the knowledge of and insight in the chemical system that is being studied. Each student in hydrochemistry should therefore have at least basic knowledge of aqueous geochemical models.

This course guide is a step by step introduction of the topic of reactive transport modelling. It is assumed that the reader has some knowledge of hydrochemistry, which is indispensible for successful application of the models. The first chapter introduces the basic theory of geochemical models and familiarizes the reader with PHREEQC by using simple example exercises. Each successive chapter discusses additional theory and the exercises increase in complexity. After having worked through the entire course guide, the student has enough theoretical background and practical experience to build his or her own models and apply these to real-world problems.

Chapter 1

Single-Species Transport

1.1 MT3DMS Exercise 1, Part 1: Single-Species 3-D Transport Simulation

The purpose of this exercise is to learn the use of MODFLOW and MT3DMS for analysis of 3-D transport of singe-species contaminants under natural-gradient hydraulic conditions. The effect of different transport solution techniques on plume migration are examined. In addition, the impact of equilibrium sorption and first-order decay will be simulated in the second part of this exercise.

1.1.1 Groundwater Flow

A sketch of the system being modeled is shown on Figure 1.1. The aquifer is confined, with a uniform thickness of 6 m that is represented by three 2 m thick layers. The model is discretized into 31 rows and 50 columns, with a regular spacing of 5 m in the *column* and *row* directions. Groundwater flow is assumed to be steady. Hydraulic heads of 18.33 m and 10.0 m are assigned along the upstream and downstream faces of the model, respectively, so that there is a uniform ambient hydraulic gradient of 0.034 along the x-axis. A uniform horizontal hydraulic conductivity of 0.864 m/d (i.e., 1×10^{-3} cm/s) is assumed, and the vertical anisotropy ratio, KV/KH, is 0.01. The resulting uniform seepage velocity is approximately 0.10 m/day.

1.1.2 Solute Transport

The contaminant source is represented by a single cell with a constant concentration of 1.0, located at row 16, column 1 in the first model layer, as shown on Figure 1.1. Clean water enters along the remaining portion of the upstream boundary. Solute is free to exit from the constant head cells along the downstream boundary. The boundary conditions along the other model faces are implicitly set as zero mass flux. The transport parameters are listed in Table 1.1 and are assumed to be uniform for all model layers.

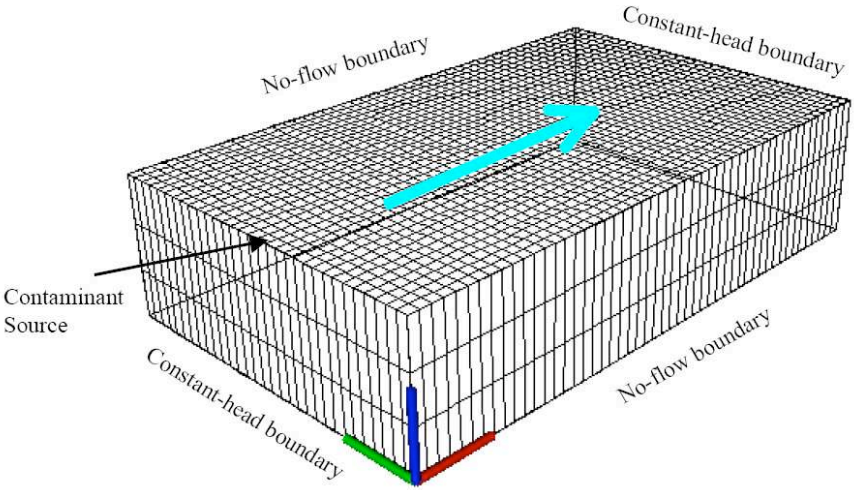


Figure 1.1: Illustration of the conceptual model and numerical model grid.

1.1.3 Setting up the flow model

To set up the flow model proceed as follows:

- In PMWIN, create a new model and save it in a new and separate directory (folder).

- Select Grid → Mesh size... to specify the model domain as described in Table 1.1. Set the model's Top elevation to 6 m.

- Select Grid → Layer property... and simply click OK. We can leave it as is but PMWIN requires that all menu entries for specifying model input are clicked.

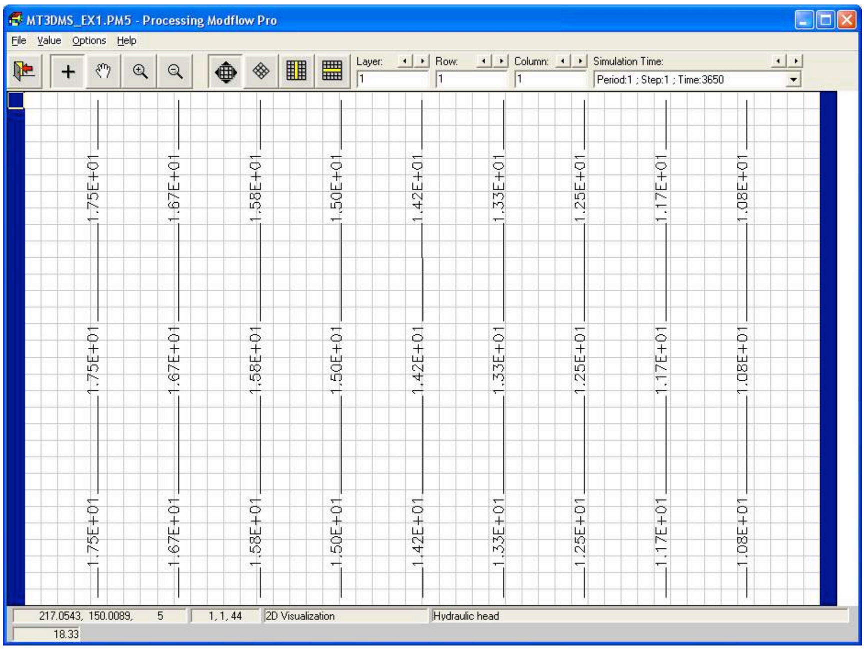
- Select Parameters → Time → and set the Simulation Time Unit to days. Then define the simulation time. Divide the total simulation time of 10 years into a first stress period of 1095 *days* (Period length) and a second stress period of 2555 *days*.

- Set the boundary conditions for heads by selecting Select Grid → Cell Status → IBOUND (Modflow). Make sure that the value of IBOUND is or becomes 1 (= active cell) at all cells, except the cells at the upstream (column 1) and the downstream boundary (column 50). Change the value of IBOUND at the upstream and downstream boundary cells to -1, which will define those cells as fixed head cells. The hydraulic heads at these grid cells will remain at the allocated values during the entire simulation. To enter the data edit the values in Layer 1. Afterwards copy the values to Layers 2 and 3. Leave the editor and save your changes.

- Select Parameters → Initial & Prescribed Hydraulic Heads → Reset Matrix and set the value to 10 m and click ok. Then change the value at all cells at the upstream boundary (column 1) to 18.33 m. Make sure that you apply these values to all three layers. Leave the editor and save your changes.
- Select Parameters → Horizontal Hydraulic Conductivity → Reset Matrix and set the value to 0.8640 m/day. Make sure that you apply these values to all three layers. Leave the editor and save your changes.
- Select Parameters → Vertical Hydraulic Conductivity → Reset Matrix and set the value to 0.00864 m/day. Make sure that you apply these values to all three layers. Leave the editor and save your changes.
- Select Parameters → Effective Porosity → Reset Matrix and set the value to 0.3. Make sure that you apply these values to all three layers. Leave the editor and save your changes.

Table 1.1: Flow and solute transport parameters used for MT3DMS Exercise 1.

Parameter	Value
Flow simulation type	steady state
Simulation time (days)	3650
Model extent column direction (m)	250
Model extent row direction (m)	155
Model thickness (m)	6
Model top elevation (m)	6
Grid spacing Δx (m)	5
Grid spacing Δy (m)	5
Number of columns	50
Number of rows	31
Number of layers	3
Horizontal hydraulic conductivity (m/day)	0.864
Vertical hydraulic conductivity (m/day)	0.00864
Porosity, θ	0.3
Piezometric head upstream boundary (m)	18.33
Piezometric head downstream boundary (m)	10
Longitudinal dispersivity, α_L	1.0 m
Horizontal transverse dispersivity, α_{TH}	0.1 m
Vertical transverse dispersivity, α_{TV}	0.01 m
Effective diffusion coefficient, D*	0



Layer: 1
Row: 1
Column: 1
Simulation Time: Period:1 ; Step:1 ; Time:3650

217.0543, 150.0089, 5
1, 1, 44
2D Visualization
Hydraulic head
18.33

Figure 1.2: Hydraulic head distribution under natural-gradient conditions.

1.1.4 Running MODFLOW

You have now completed to set up the flow model and you are ready to run MODFLOW. This step will provide MT3DMS with the flow field that is used to compute advective-dispersive transport.

- Select Models → MODFLOW → Run...
- A window appears that lists all the files that will be generated. There are also a number of options, which you can leave as they are. Click OK to start the calculations. First, PMWIN will generate the necessary MODFLOW files and then it will call MODFLOW to run the simulation model.
- When the calculation has finished, hit any key to close the command window and return to PMWIN.

1.1.5 Visualising hydraulic heads

- Visualise results by selecting Tools → 2D-Visualisation. On the MODFLOW tab select Hydraulic head and klick OK.

You should get a steady-state head distribution like shown Figure 1.2.

1.1.6 Setting up the transport model

- Set the boundary conditions for concentrations by selecting Select Grid → Cell Status → ICBUND (Trabsport models). Leave the editor without making changes. The default value for ICBUND of 1 (= active cell) will remain at all grid cells.

- Select Models → MT3DMS → Simulation Settings ... Define a new species by adding a name like Tracer to the Description list. Make it active by placing a tick mark in the box behind it and then click OK. Leave the default Type of Reaction *No kinetic reaction is simulated.*

- Define the initial concentrations by selecting Models → MT3DMS → Source/Sink Concentration → Constant Head Cells. Click Edit to start editing the concentration for the species Tracer (or any other name that you have chosen for the species). Add a pollution source by setting the Flag and the concentration value at the grid cell positioned at *Column*1, *Row* 16, *Layer* 1 to a value of 1 for the first stress period. Set the value to 0 for the second stress period. Leave the editor and save your changes.

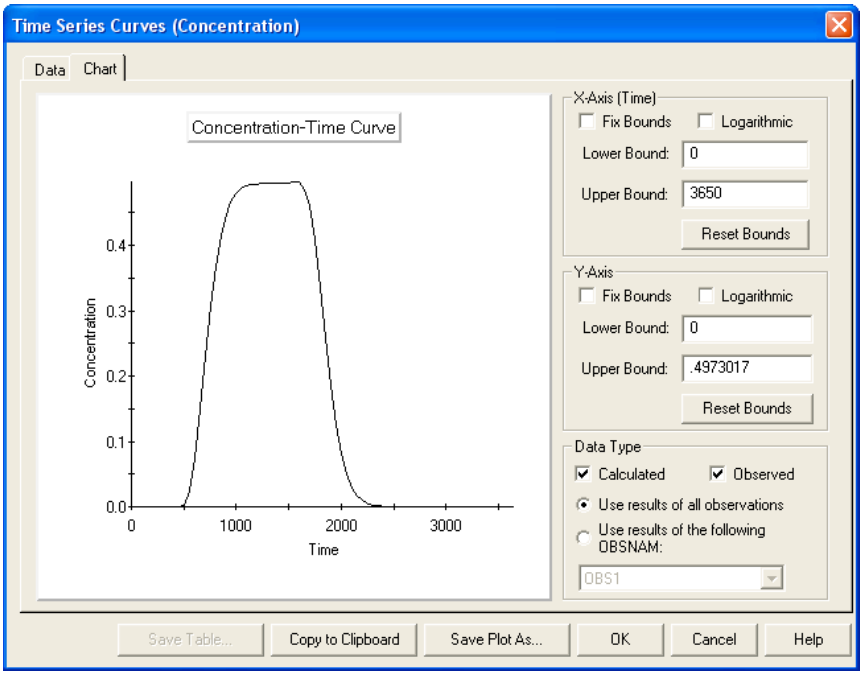
- Define the initial concentrations by selecting Models → MT3DMS → Initial Concentrations. Click Edit to start editing the initial concentration of Tracer (or any other name that you have chosen for the species). Use Reset Matrix to change the value for all initial concentrations to 0.

- Define the advection package by selecting Models → MT3DMS → Advection. Select 3rd-order TVD Scheme (ULTIMATE) as the Solution Scheme and click OK.

- Define the dispersivity to be used by selecting Models → MT3DMS → Dispersion. In the window that appears, leave TRPT at a value of 0.1. Change TRPV to 0.01 for all three layers and then click OK. In the editor, use Reset Matrix to change the value for the longitudinal dispersivity to 1.0 m. Make sure that you apply these values to all three layers. Leave the editor and save your changes.

- To visualise not only the results from the last time steps of each stress period but also some intermediate results select Models → MT3DMS → Output Control. Click on the Output Times tab and configure the settings such that results are printed every 50 days (by setting the value for Interval to 50).

- Run the transport model by selecting Models → MT3DMS → Run and clicking OK.



X-Axis (Time)
☐ Fix Bounds ☐ Logarithmic
Lower Bound: 0
Upper Bound: 3650

Y-Axis
☐ Fix Bounds ☐ Logarithmic
Lower Bound: 0
Upper Bound: .4973017

Data Type
☑ Calculated ☑ Observed
● Use results of all observations
○ Use results of the following OBSNAM:
OBS1

Figure 1.3: Concentration breakthrough curve at observation point 1 (column 16, row 16 and layer 1).

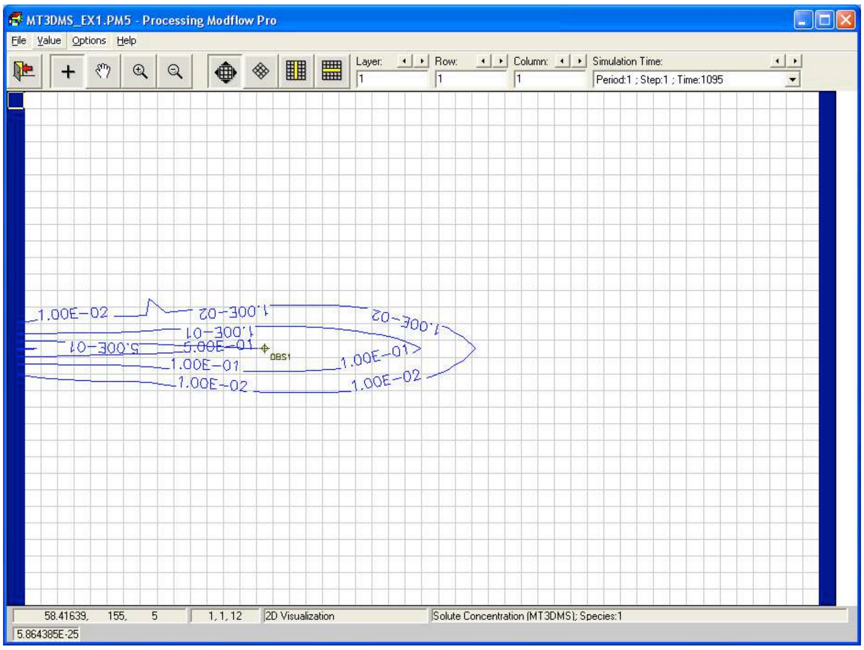
1.1.7 Breakthrough curves and contour plots

To visualise the breakthrough curve for the contaminant at a specific location proceed as follows:

- Define the observation well by selecting Models → MT3DMS → Concentration Observations. For the Observation Borehole add 77.5 as a value for X (easting) and similarely use 77.5 as value for Y (northing). Under Observation Data set the Proportion to 1 for Layer 1. Click OK.
- Visualise the breakthrough curve by selecting Models → MT3DMS → View → Concentration Time Curve. Select Tracer and click OK. Click on the Chart Tab. You can save the result as plot or you can go to the Data Tab export the data to an ASCII text file for use with another program such as Excel.

To view a contour plot of the simulated concentrations after a simulation time of 3 years

- Select Tools → 2D-Visualisation. On the MT3DMS tab select Tracer and click OK. Click on the right arrow next to Simulation Time until you have reached a value of 1095 days As you move forward in time



Layer: 1
Row: 1
Column: 1
Simulation Time: Period:1 ; Step:1 ; Time:1095

58.41639, 155, 5 | 1, 1, 12 | 2D Visualization | Solute Concentration (MT3DMS); Species:1
5.864385E-25

Figure 1.4: Calculated concentration distribution in layer 1 at year 3 under natural-gradient conditions.

you should see the contaminant plume growing (see Figure 1.4 for comparison).

- Select Options → Environment and select the Contours Tab. There you can, for example, define color ranges (Click on the Fill Tab), activate Fill contours and define the contour levels that will be displayed.
- Note, that you can easily switch over to a cross-sectional view.

1.1.8 Effect of Solution Techniques

Now let us examine the effect of transport solution techniques on the accuracy of simulation results. Export the breakthrough curve at the observation point obtained using the TVD option to an ASCII file. Then, change the advection solution option to Upstream Finite-Difference and MOC, respectively, and export the calculated concentrations to additional ASCII files. Note that dispersion and sink/source terms are always solved using the standard finite-difference method and the GCG implicit matrix solver. Use Excel to graph the three breakthrough curves. The TVD and MOC solutions are nearly identical, as both solutions have minimal numerical dispersion. The Upstream Finite-Difference solution , on the other hand, contains a significant amount of numerical dispersion. In addition, check the mass balance errors for each solution. TVD and FD should have close to zero mass balance error, while MOC has a large mass balance error at the beginning but diminishes quickly, which is typical of a particle-tracking based solution technique.

1.1.9 Optional Numerical Experiment

If you have time left, you can freely experiment with the model you have set up. For example, if you increase the longitudinal dispersivity from 1 to 5 m, and rerun the three cases , do you see all three concentration curves become nearly identical? If so, why?

1.2 MT3DMS Exercise 1, Part 2: Single-Species 3-D Transport with with Sorption and First-Order Decay

1.2.1 Linear equilibrium-controlled sorption

We use the second part of the exercise to introduce some simple reactions. Initially we only consider sorption. Proceed as follows:

- Make a copy of the folder in which the existing model is located.
- Start to add the reactions by selecting Models → MT3DMS → Chemical Reactions. Click Edit and start editing the input data. Under the Value Tab click Reset Matrix and select Linear equilibrium isotherm as sorption type. Add a value of 3×10^{-4} m^3/kg for K_d (which corresponds to 3×10^{-7} L/mg). Click OK and leave the editor.

The value to enter for K_d obviously depends on the mass and the length units that are used for the model. Those have to be consistent. Therefore the value will depend on which units will be used for the definition of the bulk densitity. With retardation being defined as

$$R = 1 + \frac{\rho_b}{\theta} K_d \tag{1.1}$$

a bulk density of 1700 m^3/kg will lead to a dimensionless retardation factor of 2.7.

To enter the bulk density

- Select Parameters → Bulk density → Cell by Cell. Go to Value → Reset Matrix and set the value to 1700 m^3/kg. Make sure that the value is applied to all three layers.
- Also, you need to select the TVD option again under the MT3DMS ŚSolution MethodŠ menu.

- Moreover, if you have changed dispersivity values, make sure to change them back to 1.0, 0.1 and 0.01 m for the longitudinal, transverse and vertical dispersivities, respectively.

- Run the MT3DMS simulation and check the concentration distribution in plan view and cross sections.

- Export the simulated concentrations for the breakthrough curve to an external ASCII file.

1.2.2 First-order Radioactive Decay or Biodegradation

Next, run another simulation with the same sorption parameters. To add a decay reaction

- Select Models → MT3DMS → Simulation Settings. Change the Type of reaction to First-order irreversible reaction.

- Then go again to Models → MT3DMS → Chemical Reactions → View → Reset Matrix. Now you can edit the first-order decay rate coefficients for both dissolved and sorbed phases to 0.00027397 $1/day$ ($=$ 0.1 $1/year$). Make sure that the value is applied to all grid cells in the model domain.

- Export the simulated concentrations for the breakthrough curve to an external ASCII file. You can then use Excel to compare your calculated breakthrough curves under different sorption and decay parameters.

Chapter 2

Calculation of a sample's equilibrium composition: Speciation and saturation indices

This chapter will be dedicated to equilibrium chemistry. The kinetics of geochemical processes, i.e., the description of how and at what rate a system approaches equilibrium, will be discussed later. The reader is also referred to the standard textbooks on aqueous geochemistry for an elaborate treatment of this subject as well as for a more detailed treatment of equilibrium chemistry (e.g. **??**).

Essential to the description of the equilibrium composition of a geochemical system is the law of mass action. According to this law, the distribution of the species in the reaction:

$$aA + bB \leftrightarrow cC + dD \tag{2.1}$$

is given at equilibrium by:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{2.2}$$

where capital characters denote the species, lowercase symbols indicate the stoichiometric coefficients and K is the *equilibrium constant*. The quantities between the brackets denote the *activity* of a species. Consider for example the dissolution of gypsum:

$$CaSO_4 \cdot 2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \tag{2.3}$$

The equilibrium constant for this reaction is given by:

$$K_{gyps} = \frac{[Ca^{2+}][SO_4^{2-}][H_2O]^2}{[CaSO_4 \cdot 2H_2O]} = 10^{-4.60} \tag{2.4}$$

which can be simplified to:

$$K_{gyps} = [Ca^{2+}][SO_4^{2-}] = 10^{-4.60} \tag{2.5}$$

since at low ionic strength (see below) the activity of water $[H_2O]$ approaches unity and the activity of a pure solid, $[CaSO_4 \cdot 2H_2O]$ in this example, equals one by definition. This expression is referred to the *solubility product* for gypsum. Note that the equilibrium constant is temperature dependent: $K_\mathrm{gyps} = 10^{-4.60}$ is valid at 25 °C.

Application of the law of mass action requires that the activities of the species are to be known. Generally, however, we are only provided with *concentrations* (because those are analyzed in the laboratory), which do not equal activities because of (1) electrostatic shielding and (2) the formation of aqueous complexes. Geochemical models can take these effects into account, which will be explained below.

2.1 Electrostatic shielding

Activities reflect the tendency of ions to react and form a precipitate (**?**). An ion in solution is surrounded by water molecules and other dissolved ions that act as a shield and reduce the reactivity of the ion. This effect can be corrected for by using a so-called activity coefficient that relates the activity of an ion to its concentration, for example Ca^{2+}:

$$[\mathrm{Ca}^{2+}] = \gamma_{\mathrm{Ca}^{2+}} \cdot \frac{m_{\mathrm{Ca}^{2+}}}{m^0_{\mathrm{Ca}^{2+}}} = \gamma^{2+}_{\mathrm{Ca}} \cdot m_{\mathrm{Ca}^{2+}} \tag{2.6}$$

where γ is the activity coefficient, which is multiplied with the concentration of the ion, $m_{\mathrm{Ca}^{2+}}$ in this example, divided by the standard state that for practical purposes conveniently equals 1 mole/kg H_2O. According to the Debije-Hückel theory, activity coefficients are a function of the *ionic strength I* of the solution:

$$I = 1/2 \sum m_\mathrm{i} \cdot z_i^2 \tag{2.7}$$

Several empirical relationships exist to calculate the activity coefficients from the ionic strength, e.g. the Davies equation at 25 °C:

$$\log \gamma_i = -0.5085 \cdot z_i^2 \left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I \right) \tag{2.8}$$

where z_i is the charge of ion i (e.g. 2 for Ca^{2+}).

Although these calculations can be awkward, they are straightforward and can still be done by hand, so the effect of electrostatic shielding is quite easily corrected for.

2.2 Formation of aqueous complexes

The second reason why the activity of an ion is lower than its concentration is that it forms aqueous complexes with other ions. Laboratory analyses

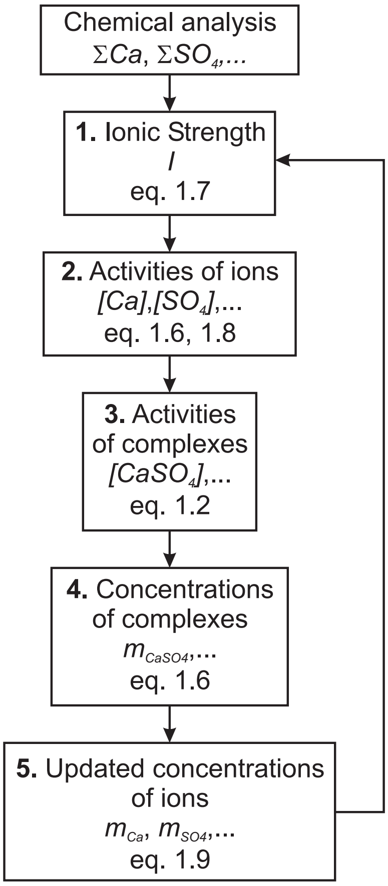


Figure 2.1: Flow chart for speciation calculations (modified from **?**)

typically report the total concentration of an ion, which may be present in many different complexes, e.g. Ca^{2+}:

$$\sum Ca^{2+} = m_{Ca^{2+}} + m_{CaOH^+} + m_{CaCO_3^0} + m_{CaSO_4^0} + m_{CaPO_4^-} + m_{CaF^+} + \dots \tag{2.9}$$

Note that these are dissolved species, they are not to be confused with minerals. Because $Ca^{2+}$is tied up in these complexes, the activity of the free calcium ion is reduced. The calculation of the concentrations of all possible species is a complex task because (1) for each ion in solution a mass balances similar to 2.9 has to be solved and (2) at the same time the activities of all of the species have to obey the equilibrium relationships that follow from the law of mass action (equation 2.2).

This requires an iterative procedure (figure 2.1). As a first estimate it is assumed that the total concentrations of the ions equal the concentrations of the free, uncomplexed ions. It is then possible to calculate the ionic strength (step 1) and use that to find the activity coefficients and correct for electrostatic effects. From this follow the activities of the ions (step 2) that are inserted into the mass action equations to obtain the activities of the aqueous complexes (step 3). These are converted to concentrations using the already calculated activity coefficients (step 4) and finally the concentrations of the uncomplexed ions are updated from the mass balance equations (step 5). The newly found values are used to obtain a more reliable value for the ionic strength and iteration continues until the result no longer changes significantly.

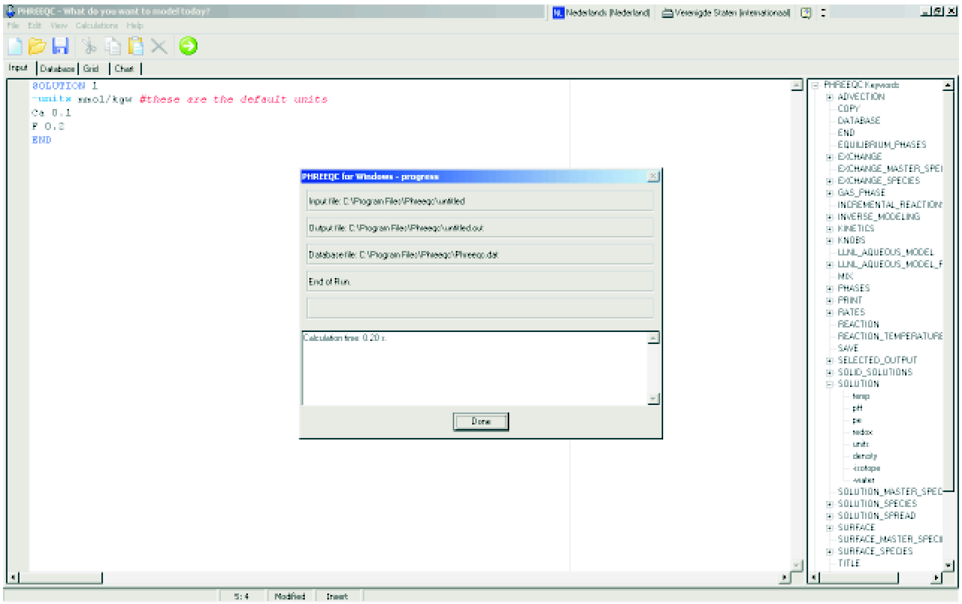
2.2.1 Your first PHREEQC input file

To do calculations, you need to tell the program what it has to do. This is done via input files that contain a list of instructions. So-called *keywords* are used that have an intuitive meaning. The keyword SOLUTION for example is used to define the (measured) composition of our water sample. Within the keyword data blocks, *identifiers* are used to set various options. For example, the identifier **-units** can be set to mg/l if the reported concentrations are in mg/l. Let's look at an example to make things more clear. Say that we have some pure water in which we have dissolved 10^{-4} moles of the mineral fluorite (so the only dissolved ions are Ca^{2+} and F^-) and we want to know the distribution of species in the water sample. This is then what your input file looks like:

```
SOLUTION 1
-units mmol/kgw # these are the default units
Ca 0.1
F 0.2
END
```

This input file tells PHREEQC that we have a solution, which is given the number 1 (the significance of these numbers will become clear later). The units of the concentrations are specified in mmol/kgw. The concentrations are simply entered after the element names. The input datablock is terminated by the keyword END, which tells PHREEQC to stop reading the input file and perform the calculations for this input datablock. The # sign indicates a comment: All text that follows on the same line is ignored when the input file is read.

To start the calculations, click Calculations → Start in the main menu or press the green arrow button on the toolbar. The program will now show a window with information on the progress of the calculations. When the calculations are finished, the caption of the button on the bottom end of this window changes from 'Cancel' to 'Done' (figure 2.2). Press it to go to the output editor where you will find the results of your calculations.



```
SOLUTION 1
-units mmol/kgw #these are the default units
Ca 0.1
F 0.2
END
```

```
Input file: C:\Program Files\Phreeqc\untitled
Output file: C:\Program Files\Phreeqc\untitled.out
Database file: C:\Program Files\Phreeqc\Phreeqc.dat
End of Run.
Calculation time: 0.20 s.
```

Figure 2.2: Screenshot of the input editor and the progress window after the calculations have finished. The panel to the right of the input editor shows the keywords and identifiers that can be used in PHREEQC.

The output file contains a lot of data and it is easy to get lost in all the numbers. The results of the speciation calculations are reported under the heading 'Beginning of initial solution calculations'. Under 'Solution composition', the molality and the number of moles of each element are reported. These should be equal to the concentrations that were entered under the SOLUTION keyword, although small deviations may occur when the mass balance (equation 2.9) could not be solved exactly. The next group of data is 'Description of solution', which lists some characteristics of the solution, for example pH and ionic strength. The molalities and activities of all the aqueous species are reported under 'Distribution of species'. Here for each element the molality is given (it is the same number as under 'Solution composition') and the molalities of each of the aqueous species of that element sum up to this molality (mass balance!). In our example it can be observed that 99.84 % of all Ca is present as uncomplexed Ca^{2+}. The remainder is present as the complexes CaF^+ and $CaOH^+$. The last block of data consists of the 'Saturation indices' calculated by the program.

2.2.2 PHREEQC Exercise 1: Cape Karoo mineral water

According to the label on the bottle, Cape Karoo mineral water derives from dolerite rock. The chemical composition of the water reflects the mineralogy of the host rock. Using the concentrations reported on the bottle label we

Figure 2.3: Label of Karoo mineral water.

can (1) check the accuracy of the chemical analysis and (2) calculate the speciation of this water.

The PHREEQC input file is given below. Only the pH (= 6.8) has not been entered yet. Look up the identifier to specify pH and enter it in the input file.

```
SOLUTION 1 Cape Karoo still
-units mg/l
... # enter pH on this line
Na 29
K 0.9
Mg 2.2
Ca 34
Cl 46
S(6) 6.8
N 0.29
F 0.72
Fe 0.08
Alkalinity 83 as CaCO3
END
```

The concentrations here are entered as mg/l. Because PHREEQC recalculates all concentrations to moles it is important to specify what molecular weights must be used for recalulating mass-based units (such as mg/l). In this case, alkalinity was reported as $CaCO_3$ and the statement 'as CaCO3' after the concentration ensures that the recaculation is done using the molecular weight of $CaCO_3$.

Redox sensitive species can have different valence states. Elemental sulfur in sulfate (SO_4^{2-}) has a valence of +6 and therefore, the element name S(6) indicates the sulfate ion. The same holds for nitrogen and iron, but because the label does not specify what form they are in, we omit the valence state. If we knew, however, that nitrogen for example was present in the form of NO_3^-, we would have entered N(5), because in NO_3^- nitrogen has a charge of +5.

Another special case is HCO_3^-, which can not be entered directly but is specified here as Alkalinity (note that element names are case sensitive). In natural waters were the alkalinity comes from carbonate species, this is a valid assumption. The different options for specifying TIC, alkalinity and pH are listed in appendix I.

- What is the percent error of the electrical balance of this chemical analysis? Answer: .... Because its absolute value is less than 5 % we may conclude that the analysis is acceptable.
- The label lists no concentration for silica, Si. How would the calculation of the electrical balance change if we include this element?
- How much is the ionic strength (equation 2.7) that PHREEQC has calculated? Answer: $I = \ldots\ldots\ldots$
- What are the 2 most dominant Ca^{2+} species and their concentrations? Answer:

    1. ......, concentration = ...,
    2. ......, concentration = ...

2.3 Saturation state

The saturation index is an important parameter in aqueous geochemistry as it provides information on the minerals the groundwater has been in contact with and on which minerals are likely to precipitate or dissolve.

An expression analogue to equation 2.5 can be written that uses the actual activities of the species in the groundwater instead of the activities at equilibrium, which is referred to as the *ion activity product* (IAP):

$$IAP_{\text{gyps}} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] \tag{2.10}$$

A comparison of IAP and K provides information on the saturation state of the groundwater for a mineral. This is commonly done by calculating the *saturation index* (SI), for example for gypsum:

$$SI_{\text{gyps}} = \log\left(\frac{IAP_{\text{gyps}}}{K_{\text{gyps}}}\right) \tag{2.11}$$

At equilibrium IAP_{gyps} equals K_{gyps}, so $SI_{\text{gyps}} = 0$. Gypsum potentially dissolves in groundwater that is subsaturated (i.e. $SI_{\text{gyps}} < 0$) or precipitates from groundwater that is supersaturated (i.e. $SI_{\text{gyps}} > 0$).

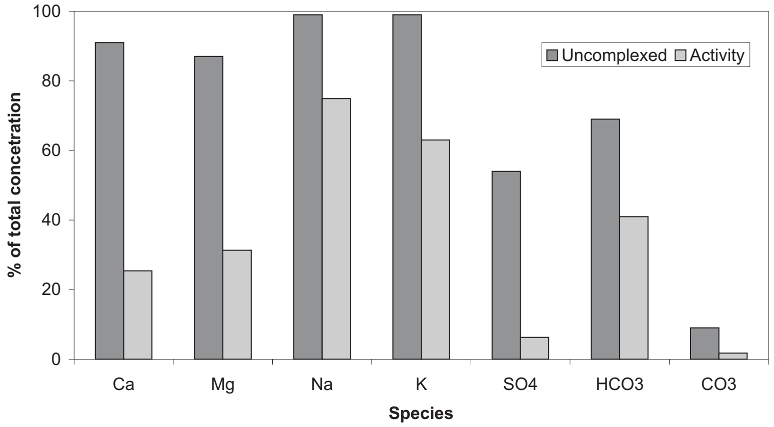


Figure 2.4: Effect of complexation and electrostatic shielding expressed as percentage of total concentration. Based on calculations by **?**.

2.3.1 Calcite saturation state of seawater

The basic principles of calculating a water's composition at equilibrium were presented in a landmark paper by **?** and the theoretical framework presented therein continues to be applied in present-day geochemical models. Using a combination of equilibrium equations from the law of mass action and mass balance relations (as explained in the previous section), they calculated the distribution of dissolved species (speciation) in seawater at 25 °C and $1.013 \cdot 10^5$ Pa (1 atm) pressure. Their results have been summarized in Figure 2.4, which shows the effects of both (1) the formation of aqueous complexes and (2) electrostatic shielding. Sodium (Na^+), for example, hardly forms any aqueous complex but due to electrostatic effects its activity amounts to only 75 % of its total concentration. More than 90 % of the carbonate ion (CO_3^{2-}) is tied up in a complex and it can be seen that its activity amounts to a mere 2 % of its total concentration when the effect of electrostatic shielding is taken into account as well.

Clearly, neglecting the difference between total concentration and activity in the calculation of the saturation indices of seawater for minerals would result in overprediction of the values. The following PHREEQC input file repeats the calculations by **?** to calculate the saturation index for calcite in seawater, using the seawater composition which is taken from example 1 in the user's manual of PHREEQC (**?**):

```
SOLUTION 1 Seawater
units ppm
pH 8.22
temp 25.0
Ca 412.3
```

```
Mg 1291.8
Na 10768.0
K 399.1
Cl 19353.0
Alkalinity 141.682 as HCO3
S(6) 2712.0
END
```

You can run this input file and verify that the total concentrations of Ca^{2+} and CO_3^{2-} amount to $m_{Ca^{2+}} = 9.504 \cdot 10^{-3}$ and $m_{CO_3^{2-}} = 3.826 \cdot 10^{-5}$ mol/kgw, respectively. The corresponding activities are $[Ca^{2+}] = 2.380 \cdot 10^{-3}$ and $[CO_3^{2-}] = 7.969 \cdot 10^{-6}$ mol/kgw, respectively. Inserting the activities in the expression for the saturation index (equation 2.11) yields:

$$SI_{\text{calcite}} = \log\left(\frac{IAP_{\text{calcite}}}{K_{\text{calcite}}}\right) = \log\left(\frac{[2.380 \cdot 10^{-3}][7.969 \cdot 10^{-6}]}{10^{-8.48}}\right) = 0.76 \tag{2.12}$$

which is the value that is reported by PHREEQC for calcite in under the heading ‘Saturation indices’. Note that if the concentrations of the species had been used instead of the activities, the calculated saturation index would be $SI_{calcite} = 2.04$, which is much too high.

2.3.2 PHREEQC Exercise 2: Fluoride-rich waters

Fluorite is a common mineral in volcanic rocks and an important source of fluoride in groundwater. High fluoride concentration in drinking water are known to cause fluorosis, a painful crippling disease. That is why the WHO drinking water standard is 1.5 mg/l, although this may even be too high for arid areas where people consume a lot of water.

Table 2.1: Examples of fluoride-rich waters. Concentrations are in mmol/l, except pH.

	A: Maarum, Denmark	B: Rajasthan, India	C: Lake Abiata, Kenya
pH	7.8	7.3	9.62
Na^+	19.1	47.9	194
K^+	0.36	0.15	4.91
Mg^{2+}	1.19	0.79	0.02
Ca^{2+}	1.05	0.68	0.042
Cl^-	5.67	17.4	53.9
HCO_3^-	17.8	14.8	138
SO_4^{2-}	0.0	5.2	0.15
NO_3^-	0.03	7.8	-
F^-	0.089	0.356	6.28

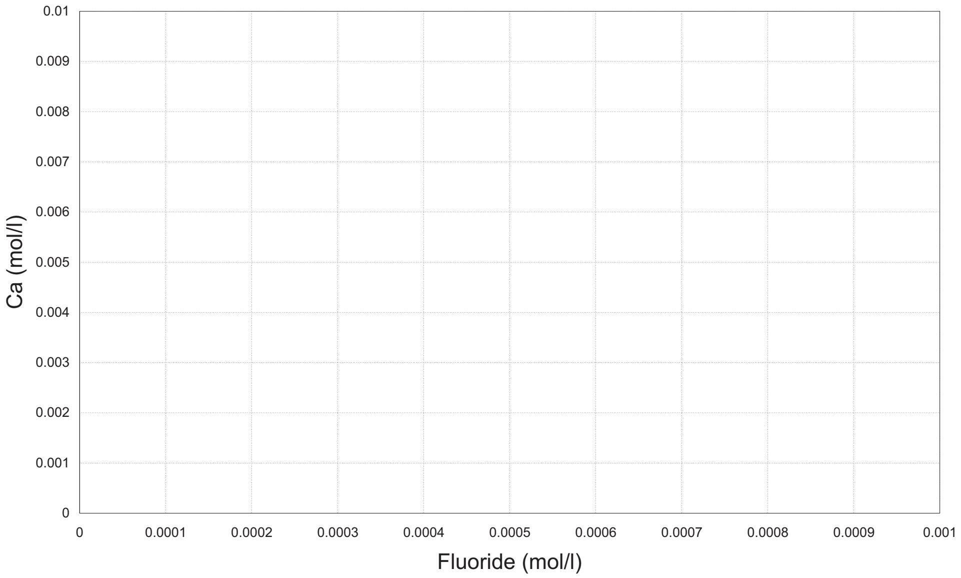


Figure 2.5: Plot of Calcium vs. Fluoride concentrations.

- Calculate the saturation index (SI) of the water samples in table 2.1 for fluorite ($CaF_2 \leftrightarrow Ca^{2+} + 2F^-$, $K_{fluorite} = 10^{-10.6}$), without making corrections for the ionic strength and complexes.

  Results:

  $SI_{fluorite,A} = \ldots\ldots$, $SI_{fluorite,B} = \ldots\ldots$, $SI_{fluorite,C} = \ldots\ldots$

- Calculate $SI_{fluorite}$ with PHREEQC. The input file is available as *fluorite1.phrq*. The concentrations of the elements are entered under SOLUTION. Remember that NO_3^- is entered as N(5) and SO_4^{2-} as S(6).

  Browse through the output file to find the saturation indices of each of the water samples:

  $SI_{fluorite,A} = \ldots\ldots$, $SI_{fluorite,B} = \ldots\ldots$, $SI_{fluorite,C} = \ldots\ldots$

- Why is there a difference between hand- and computer calculations?

- Use figure 2.5 to make a plot of the concentration of Ca^{2+} against the concentration of F^-.

- Calculate the Ca^{2+} concentration of water in equilibrium with fluorite at a F^- concentration of:

- Use the values from the table above to plot the equilibrium-line for fluorite in the graph.

Sample	F^-	Ca^{2+}(mol/l)
1	$5.264 \cdot 10^{-5}$ mol/l (= 1.0 mg/l)	......
2	$7.895 \cdot 10^{-5}$ mol/l (= 1.5 mg/l)	......
3	$1.579 \cdot 10^{-4}$ mol/l (= 3.0 mg/l)	......

Samples that plot on the solubility curve are in equilibrium with fluorite. Samples that plot above or below the curve are super- and subsaturated, respectively.

- Will a 1:1 mixture of samples 1 and 3 be in equilibrium, super- or subsaturated with respect to fluorite?
- In the hand calculations the difference between concentration and activity is not taken into account. A more accurate calculation is done with PHREEQC. The basic set-up of the input file is given in *fluorite2.phrq*. Open it in the editor, fill in the missing numbers and run it.

Sample	F^-	Ca^{2+}(mol/l)	ratio hand/computer
1	$5.264 \cdot 10^{-5}$ mol/l (= 1.0 mg/l)	......	......
2	$7.895 \cdot 10^{-5}$ mol/l (= 1.5 mg/l)	......	......
3	$1.579 \cdot 10^{-4}$ mol/l (= 3.0 mg/l)	......	......

- Why does the ratio between hand and computer calculated concentrations change?
- How much fluorite precipitates/dissolves in the 1:1 mixture of samples 1 and 3?

Chapter 3

Mineral dissolution and precipitation

3.1 PHT3D Exercise 1: Transport and mineral reactions

The present exercise is the first PHT3D application example. Building on the experience gained from the first PHREEQC examples, it combines a simple one-dimensional flow/mass transport simulation with mineral precipitation/dissolution reactions.

The case simulated in this exercise was originally presented by **?** for a model verification of their MST1D code against the CHEMTRNS model by **?**. It involves a one-dimensional model domain in which an aqueous water composition that is in equilibrium with two minerals, calcite and dolomite, is successively replaced, i.e., flushed by water of a different chemical composition, leading to multiple precipitation-dissolution fronts. Dolomite is not present initially but is formed temporally.

3.1.1 Spatial discretisation and flow problem

In order to exactly reproduce the discretisation chosen by **?**, the total length of the model domain must be set to 0.5 m and subdivided into 50 grid cells of 0.01 m length. Each of these cells has a width of 1 m and also a height of 1 m height. With this discretisation the model has 50 columns, 1 row and 1 layer. The total simulation time is 0.24305 days. The temporal discretisation (time step length) is set to 0.01 day.

With the selected model dimensions a steady-state flow rate Q_{well} of 0.259 m^3 d^{-1} is required to achieve the pore-velocity of 0.81 m d^{-1} (as defined by **?**) for a porosity of 0.32. A summary of the parameters that define the flow field and the non-reactive transport simulation is given in Table 3.1.

To implement this model setup into iPHT3D proceed as follows:

- In iPHT3D, create a new model and save it in a new and separate directory to avoid any mixup of different models and model results.

- Under Parameters → Model select the Grid button and specify the model domain in the dialog that opens up. Use the values as discussed above and listed in Table 3.1.
- Under Parameters → select the Time button to define the simulation time of 0.2435 days under Total Simulation Time and the Step Size to a value of 0.01 day
- Go to Spatial Attributes → MODFLOW → DIS → dis.6 Top of Layers (TOP) and set the top of the model to 1 m. Don't forget to validate the input by clicking the ok button.
- Go to Spatial Attributes → MODFLOW → DIS → dis.7 Bottom of Layers (BOT) and set the value to 0 m (the default value).
- Set the boundary conditions for heads by going to Spatial Attributes → MODFLOW → BAS6 → bas.3 Boundary Conditions and setting the value to 1 (= active cell) for all cells. After that select Zone and use the Zone Tools to add a line at the last cell, which represents the downstream boundary. The value of the zone needs to be set to -1 (fixed head). This will define a fixed head boundary, i.e., the hydraulic head at this grid cell will remain at the value that will be defined as initial head.
- Set initial hydraulic heads by going to Spatial Attributes → MODFLOW → BAS6 → bas.5 Initial Heads and set one_value to 1. The initial heads will be used by MODFLOW as initial estimates for solving the flow equations. During the solution procedure the correct heads will be computed. At locations for which a fixed head boundary condition was defined the heads will remain unchanged, as discussed above.

Table 3.1: Flow and transport parameters used in PHT3D Exercise 1.

Flow simulation	steady state
Total simulation time (*days*)	0.24305
Time step (*days*)	0.01
Grid spacing (*m*)	0.01
Model length (*m*)	0.50
Pore velocity (*m*/*day*)	0.81
Hydraulic conductivity (*m*/*day*)	1
Effective Porosity (−)	0.32
Total Porosity (−)	0.32
Dispersivity (*m*)	0.0067

- Go to Spatial Attributes → MODFLOW → LPF → lpf.8 to specify the hydraulic conductivity to 1 m/day
- Go to Spatial Attributes → MODFLOW → WEL and add a zone Well and set the flow rate of the first cell, i.e., the cell representing the inflow end of the model, to 0.259 m^3/day.

3.1.2 Running MODFLOW

You have now completed to set up the flow model and you are ready to run MODFLOW. This step will provide PHT3D with the flow field that is used to compute advective-dispersive transport of mobile species/components:

- Under Parameters → Flow use the Pencil Button to write all the input files required to run MODFLOW
- Under Parameters → Flow use the Red Arrow button to start the MODFLOW simulation

During the execution of MODFLOW a number of output files are created, including the specific file **mt3d.flo**, which contains the flow vectors of each cell for each time step in the simulation. This file is required for the subsequent PHT3D simulation(s) and PHT3D will not run until the file **mt3d.flo** exists. If changes are made to the MODFLOW input parameters MODFLOW needs to be rerun such that the file **mt3d.flo** is updated.

3.1.3 PHT3D reaction definition

We continue now with the setup of the reactive transport model. In some cases the next step would be to prepare a problem-specific reaction module. However, for simpler problems such as the one in this exercise and many others that only include equilibrium reactions, this is not the case. All of the aqueous species, components and minerals needed to simulate this LEA-based reactive transport problem are already included in the original PHREEQC-2 database. This means that we don't have to define our own set of equilibrium reactions but we can simply use a PHT3D database file that is equivalent to the original PHREEQC-2 database. To specify this and to incorporate the correct reaction database, proceed as follows:

- Copy the database file that is going to be used for the PHT3D simulation into the folder that contains all files for this exercise and name the file **pht3d_datab.dat**.
- Go to Parameters → Chemistry and select the Import database button. iPHT3D will then read and interpret the PHT3D database file.

- Then click on the Chemical Reaction button. This will open up a new dialog box
- Within the new dialog box go to the Solution Tab and select the aqueous components that you want to include in the model. In this exercise the simulation needs to include C(4), Ca, Cl, Mg, pe and pH.
- Then click the Phases Tab and select (i.e., activate) the two minerals Calcite and Dolomite.

These steps are the only steps needed to define the set of chemical reactions that will be considered in the PHT3D simulation. From this information iPHT3D will create the interface file that controls the communication between the MT3DMS part and the PHREEQC-2 part of the PHT3D simulator. This file, **pht3d_ph.dat**, contains the records which define that the reaction network contains 6 equilibrium aqueous components (including pH and pe) and two equilibrium minerals. The order in which the components are listed determines which species number will be allocated to each entity included in the simulation. For each of the first **MCOMP**-2 (C(4)), Ca, Mg, Cl) of the **NCOMP** components advective-dispersive transport steps will be simulated by the appropriate MT3DMS routines. For component numbers **MCOMP**-1 (pH) and **MCOMP** (pe) no transport step is carried out. The entities **MCOMP** + 1, ... ,**NCOMP** (here Calcite and Dolomite) are immobile and no transport simulation will be carried out for them.

3.1.4 Initial and inflow concentrations

The next step in setting up this problem is to specify the initial concentrations that define the hydrogeochemistry of the aquifer at the start of the simulation (Time = 0). The information provided here will be translated by ipht3d into the the basic transport package file, which is called **pht3dbtn.dat** in PHT3D. The initial concentrations that need to be entered into iPHT3D, as defined in the paper by **?**, are listed in Table 3.2 (for aqueous components) and in Table 3.3 (for minerals).

Note, that aqueous concentrations are always defined in units of $mol\ l^{-1}$**. In contrast, the unit for the initial concentrations of minerals is NOT mass per volume of water, i.e.,** $mol\ l^{-1}$**, but is defined as mass per bulk volume, i.e.,** $mol\ l^{-1}_{volume}$.

? defined their mineral concentrations as mass per mass of soil, i.e., $mol\ kg^{-1}_{soil}$ and provided the bulk density (1800 $kg\ m^{-3}$) of the soil. Therefore, their initial concentrations for calcite of $2.176 \times 10^{-5}\ mol\ kg^{-1}_{soil}$ translates to $3.906 \times 10^{-5}\ mol\ l^{-1}_{volume}$, which needs to be used in PHT3D.

If a simulation problem, like the one we are simulating here, is a pure equilibrium problem, it should be warranted that the initial water composition is in chemical equilibrium and the aqueous solution is charge-balanced. If the aqueous solution is not in equilibrium, equilibrium conditions will be adjusted within the first reaction step at the end of the first time step. This can cause an undesired change, for example, of the solution pH or the dissolution/precipitation of minerals. To avoid this it is recommended to study and charge-balance the aqueous solution with PHREEQC before entering the data into iPHT3D.

Table 3.2: Aqueous concentrations used in PHT3D Exercise 1.

Aqueous component	C_{init} $(mol\ l_w^{-1})$	C_{inflow} $(mol\ l_w^{-1})$
pH	9.91	7.0
pe	4.0	4.0
C(4)	1.23×10^{-4}	0.0
Ca	1.23×10^{-4}	0.0
Mg	0.0	1.0×10^{-3}
Cl	0.0	2.0×10^{-3}

Table 3.3: Mineral concentrations used in PHT3D Exercise 1.

Mineral	C_{init} $(mol\ l_v^{-1})$
Calcite $(CaCO_3)$	3.906×10^{-5}
Dolomite $(CaMg(CO_3)_2)$	0.0

There are various ways and types of boundary conditions to define the hydrochemical composition of water that is entering the model domain during a simulation. In the present case the inlet (inflow) water composition is defined by providing the aqueous component concentrations for the injection well located at the first cell. The inlet water contains 0.001 $mol\ l^{-1}$ of Mg and 0.002 $mol\ l^{-1}$ of Cl. In contrast to the initial water composition, no C(4) and no Ca is contained in the inflow water. You can enter these values (see also Table 3.2) into iPHT3D as follows:

To define both the initial and inflow concentrations you will enter the chemical composition of the respective aqueous solutions. In this exercise the background contains water that is in chemical equilibrium with the mineral *Calcite*. The composition of the initial water needs to be entered under the

Solutions Tab in the Background column. On the other hand the initial mineral composition must be entered under the Phase Tab (with the value of the saturation index (SI) and the initial concentration in the assemblage). Leave the SI at the default value of 0, as would be the case for most typical model applications. The inflow water composition will be defined in the Solution 1 column under the Solutions Tab.

To additionally define that the inflow composition is used at the correct location (i.e., the inflow boundary) we need to select Spatial Attributes → PHT3D → PH → ph.4 Source Sink and define a zone (point) near the inflow boundary and allocate a Zone Value of 1. This induces that the previously defined concentrations for Solution 1 (as defined in the Solutions Tab) will be used to specify the concentrations in the water that enters the column.

3.1.5 Data input for solute transport

For the simulation of solute transport of the mobile components you need to specify the model parameters that control advective and dispersive transport. It is assumed that the parameters that define the physical transport of the chemicals are the same for every species/component:

- Go to Parameters → Transport and select the Parameter button
- In the dialog box that subsequently appears, select ADV and the 3rd-order TVD Scheme (ULTIMATE) as the Solution Scheme and click OK.
- Select Spatial Attributes → MT3DMS → DSP, enter a longitudinal dispersivity value of 0.0067 m. and click ok
- Leave the values for the dispersivity ratios and diffusion coefficients as they are and click OK.
- Go to Spatial Attributes → MT3DMS → BTN → (btn.11) and specify the effective porosity to be 0.32.

3.1.6 Running PHT3D

To run PHT3D, proceed as earlier in the exercise when executing MODFLOW:

- Go to Parameters → Chemistry and use the Pencil Button to write all the input files required to run PHT3D
- Then go to Parameters → Chemistry and use the Plume Button to start PHT3D.

3.1.7 Visualization of simulation results

To visualise the simulation results and to compare them with the results we need to extract the simulated concentrations in the form of concentration profiles for the end of the simulation time. This can be achieved by creating a so-called observation zone. This option can be used to display the results graphically but also to export the results and save them in newly created data files.

- Select Spatial Attributes → Observation → OBS → obs.1 → Zone and create a zone as a horizontal line that maybe named *line*1. No additional input is needed here.
- In the Results Panel select the final time step of the simulation by going to Results → Aquifer → Tstep and selecting 0.24305 days
- In the Results sub-panel select one of the specific species that you want to visualise by going to Results → Chemistry → Species and selecting, for example, Ca.
- Then go to Results → Observation and select the visualisation type Profile. Then select the Profile option
- in the following dialog you can either select a single or multiple species. For pure visualisation the selection of multiple species makes only sense for all those species which prevail within the same concentration range. However, in this exercise we want to export the data for multiple species and therefore we select all of the simulated species
- Once the species are selected a new dialog will open. This new dialogue allows to make a selection among several types of concentration averaging techniques. In the present case simply select the default option, i.e., Value
- Now a plot should appear that shows the simulated concentrations of all selected species along the previously defined *line*1, i.e., concentration profiles along the column should show up
- You can now use the Export button to export the simulated values into a text file.

3.1.8 Comparison of simulation results

If all steps of the model definition were performed correctly the results should agree closely with those otained by **?**, as illustrated in Figure 3.1. Generally the simulated concentrations, including the positions of the mineral fronts agree very well. However, the PHT3D-simulated pH near the inflow end of the model domain lies slightly above the pH simulated by MST1D.

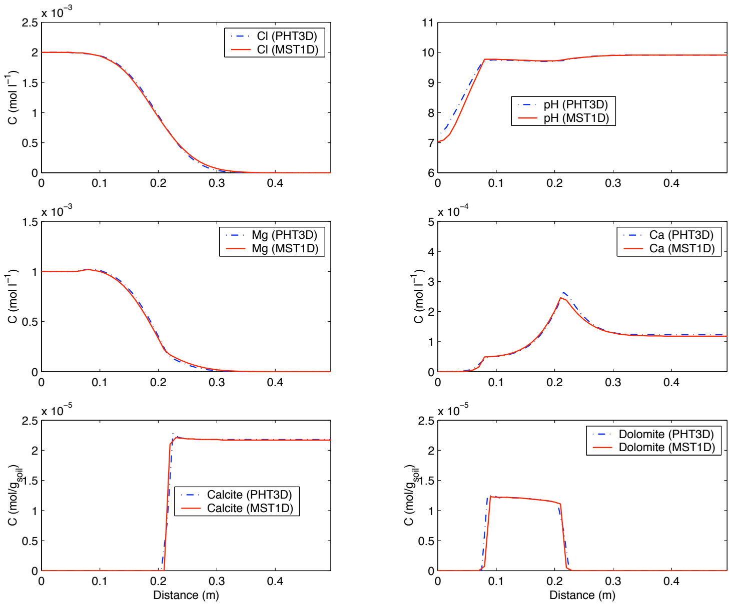


Figure 3.1: Simulation results for PHT3D and MST1D: Aqueous and mineral concentrations after 21000 s.

Table 3.4: Flow and transport parameters for the simulation.

Flow simulation	steady state
Total simulation period (*days*)	2000
Model length (m)	100
Model thickness (m)	10
Grid spacing Δx (m)	4
Grid spacing Δz (m)	1
Porosity	0.35
Horizontal hydraulic conductivity (m/day)	1
Vertical hydraulic conductivity (m/day)	1
Piezometric head upstream boundary (m)	12
Piezometric head downstream boundary (m)	10
Longitudinal dispersivity (m)	0.5
Transversal dispersivity (m)	0.05

3.2 PHT3D Exercise 2: Precipitation/dissolution fronts in acid mine drainage

This exercise is a second simulation problem that involves mineral dissolution and precipitation reactions as the principle geochemical reactions. Compared to the first exercise it is somewhat more complicated as it contains significantly more aqueous components and mineral reactions. Those also occur now in a slightly more complex flow field. It was first presented by **?** and later also used as a benchmark problem by **?**. In contrast to the previous exercise this case includes now also redox reactions. The simulations demonstrate the typical hydrogeochemical changes that occur when acidic mine tailings leach into an anaerobic carbonate aquifer. Aqueous complexation and dissolution/precipitation are all considered as equilibrium reactions. If the original reaction network defined by **?** is used, the simulation includes 17 aqueous components, 15 of which are transported, 54 aqueous species and six minerals.

3.2.1 Spatial discretisation and flow problem

The problem is set up as a simple two-dimensional flow and transport problem with dimensions and properties as defined in 3.4. To construct the MODFLOW model that underlies the transport problem proceed as follows:

- In iPHT3D, create a new model and save it again in a new, separate directory.

- Under Parameters → Model select the Model button and specify the attributes of the new model. Select the values Xsection for Dimension, Confined for Type and MODFLOW Family for Group

- Under Parameters → Model select the Grid button and specify the details of the model domain and the spatial discretisation in the dialog that opens up. Define a vertical transect that is 100m long and 10m thick. The model domain may be discretised into grid cells of 4m length and 1m thickness. Note, that the model discretisation can be easily changed again later.

- Select Parameters and select the Time button. Set the Total Simulation Time to 2000 days and select a time Step size of 20 days.

- Go to Spatial Attributes → MODFLOW → LPF → lpf.8 to specify the hydraulic conductivity to 1 m/day

- Go to Spatial Attributes → MODFLOW → LPF → lpf.9 to specify the vertical hydraulic conductivity to 1 m/day

- Go to Spatial Attributes → MT3DMS → BTN → btn.11 and specify the effective porosity to be 0.35.

- Implement hydraulic boundary conditions by defining the hydraulic heads at the upstream and the downstream boundary of the model. First, define the type of boundary condition by going to Spatial Attributes → MODFLOW → BAS6 → bas.3 Boundary Conditions and setting the value to 1 (= active cell) for all cells. After that select Zone and use the Zone Tools to add one line at the inflow end of the model and one line at the effluent end. In both cases the lines need to extend over the whole depth of the aquifer. The value for both lines (=zones) needs to be set to -1. Use, for example, *bc_up* and *bc_down* as Zone Names. You will see the selected names displayed near the location of the lines.

  This will define a the type of boundary condition to a fixed head boundary at the inflow and outflow model boundaries. The hydraulic head at these grid cells will therefore remain unchanged over the whole simulation period. It will remain at the same values that we will now define as initial heads.

- Set initial hydraulic heads by going to Spatial Attributes → MODFLOW → BAS6 → bas.6 Initial Heads and set one_value to 10, corresponding to a head of 10m. Then press ok to confirm the value. In addition define a zone (line) at the upstream end of the model domain (where you also defined that the type of boundary condition is -1) and allocate a hydraulic head of 12m over the entire depth of the aquifer.

3.2.2 Running MODFLOW

You have now completed to set up the flow model and you are ready to run MODFLOW.

- Under Parameters → Flow use the Pencil Button to write all the input files required to run MODFLOW
- Under Parameters → Flow use the Red Arrow button to start the MODFLOW simulation
- Check the simulated head contours and assess whether the results are plausible.

3.2.3 Data input for solute transport properties

For the simulation of the solute transport of the mobile components the model parameters that control advective and dispersive transport need to be entered.

- Go to Parameters → Transport and select the Parameter button
- In the dialog box that subsequently appears, select ADV and select under adv.1 Solver Parameters the 3rd-order TVD Scheme (ULTIMATE) as the Solution Scheme. Leave the default parameters and click ok.
- Select Spatial Attributes → MT3DMS → DSP, enter a longitudinal dispersivity value of 2.5 m. and click OK
- Select Spatial Attributes → MT3DMS → DSP, and specify that the ratio between transverse vertical dispersivity and the longitudinal dispersivity is 0.01. This will define that the actual value is 0.025 m (= 25mm).

3.2.4 Data input for reactive transport

In this step we define the reaction network and the various water and mineral compositions that play a role in this problem. Both the initial and the inflow concentrations of of the aqueous components that will be used in the simulation are shown in Table 3.5. Also the initial concentrations of the minerals are given in Table 3.6.

- Copy the database file that is going to be used for the PHT3D simulation into the folder that contains all files for this exercise and name the file **pht3d_datab.dat**. You can use the same dataase as in PHT3D Exercise 1, i.e., the standard PHREEQC database.

- Go to Parameters → Chemistry and select the Import database button. iPHT3D will then read and interpret the PHT3D database file.

- In this next step we define all initial concentrations of all aqueous components and minerals and also the concentrations at the upstream model boundary (which will be allocated to the inflowing groundwater).

  The composition of the ambient water (initial water composition at the start of the simulation) needs to be entered under the Solutions Tab in the Background column. Activate all relevant species by ticking the appropriate boxes for pH, pe, $C(4)$, $S(6)$, $S(-2)$, $Fe(2)$, $Fe(3)$, $Mn(2)$, Ca, Mg, Na, Cl, Al and Si and enter the concentrations. The set of minerals that are considered in this simulation must be activated and the corresponding mineral composition must be entered under the Phase Tab.

  In addition to the background water composition we will also need to define the composition of the acidic tailings water that enters the model domain in the upper section of the upstream boundary. This water composition will be defined in the Solution 1 column under the Solutions Tab. For the lower section of the inflow boundary it is assumed that the inflowing water is the same as the background water composition.

- The allocation of the appropriate water compositions as model boundary condition can be done by selecting Spatial Attributes → MT3DMS → BTN → btn.12 Boundary Condition and defining a zone (line) for the lower section of the inflow (upstream) boundary (between y = 0m and y = 7m) for which a value of -1 is allocated. This defines that the concentrations at these grid cells will not change during the entire simulation. The concentrations that iPHT3D will allocate to the model's grid cells are the ones defined as initial concentrations. This means that the water composition that was defined as background water composition will also be used as inflow water composition.

  To additionally define that the acidic leachate composition is used in the upper section we need to select Spatial Attributes → PHT3D → PH → ph.4 Source Sink and define a zone (line) for the uppermost 3 m (y= 7m to y = 10m) of the boundary (the depth zone at which the acidic leachate enters) and allocate a Zone Value of 1. This induces that the concentrations that were previously defined for *Solution* 1 in the Solutions Tab will be applied to the water that enters the model domain in the upper section of the inflow boundary.

3.2.5 Running PHT3D

To run PHT3D, proceed as earlier in the exercise when executing MODFLOW:

- Go to Parameters → Chemistry and use the Pencil Button to write all the input files required to run PHT3D
- Then go to Parameters → Chemistry and use the Plume Button to start PHT3D.

3.2.6 Visualisation of results

After the end of the simulation visualise the results in various ways.

- Obtain a contour plot by navigating in the Results panel of ipht3d. Select a specific timestep and a species for which you want to see your results. For example to see the pH contours after 1000 days select Results → Aquifer → Tstep and select 1000 and then go to Results → Chemistry → Species and select pH. You can easily move forward and backward in time by clicking Tstep once more and then using your keyboard arrows to move forward or backward.
- Plot a breakthrough curve at a selected location to visualise how concentrations change over time. First, define the location for which you want to plot breakthrough curves by going to Spatial Attributes → Observation → OBS → obs.1 → Zone and use your mouse to position the cursor and clicking at the location where you wan to create an observation point. In the dialog that comes up name the zone $BTC1$. No specific input is required for the Zone Value field. The coordinates of the location selected by the mouse click can be modified, if required.

3.2.7 Discussion of simulation results

Only a few aspects of the geochemical evolution observed in the model simulation are described in the following. For a detailed description see **?**. The acidic inflow solution is initially buffered by calcite ($CaCO_3$), maintaining the pH at an almost neutral level (6.5 - 7). In this zone, gypsum ($CaSO_4.2H_2O$) is formed from calcium released during calcite dissolution and sulphate ($S(6)$) from the inflow solution ($C_{in,S(6)} > C_{backgr,S(6)}$). Similarly, siderite ($FeCO_3$) can form from $C(4)$ (CO_3) released during dissolution and the $Fe(2)$-rich inflow solution. At locations where calcite is completely dissolved, siderite becomes the buffering mineral, dissolving until it is also entirely removed. Finally, gibbsite ($Al(OH)_3$) precipitation is the buffer

Table 3.5: Aqueous concentrations used in the Walter et al. Example.

Aqueous component	C_{init} $(mol\ l_w^{-1})$	$C_{tailing}$ $(mol\ l_w^{-1})$
pH	6.96	3.99
pe	1.67	7.69
C(4)	3.94×10^{-3}	4.92×10^{-4}
S(6)	7.48×10^{-3}	5.00×10^{-2}
S(-2)	-	-
Fe(2)	5.39×10^{-5}	3.06×10^{-2}
Fe(3)	2.32×10^{-8}	1.99×10^{-7}
Mn(2)	4.73×10^{-5}	9.83×10^{-6}
Ca	6.92×10^{-3}	1.08×10^{-2}
Mg	1.96×10^{-3}	9.69×10^{-4}
Na	1.30×10^{-3}	1.39×10^{-3}
K	6.65×10^{-5}	7.93×10^{-4}
Cl	1.03×10^{-3}	1.19×10^{-4}
Al	1.27×10^{-7}	4.30×10^{-3}
Si	1.94×10^{-3}	2.08×10^{-3}

Table 3.6: Mineral concentrations Walter et al. Example.

Mineral	C_{init} $(mol\ l_v^{-1})$
Calcite $(CaCO_3)$	1.95×10^{-2}
Siderite $(FeCO_3)$	4.22×10^{-3}
Gibbsite $(Al(OH)_3)$	2.51×10^{-3}
amorphous $Fe(OH)_3$	1.86×10^{-3}
Gypsum $(CaSO_4.2H_2O)$	0.0
amorphous SiO_2	4.07×10^{-1}

mechanism at locations where both calcite and siderite are completely removed. The three different buffering mechanisms lead to three distinct levels of pH. Also three distinct pe levels evolve with fronts from more reduced to more oxidised water. The fronts have the same positions as those in the pH plot. As the pe of the solution is completely controlled by the redox couple $Fe(2)/Fe(3)$, the pe changes reflect the changes in their concentration ratio. Both $Fe(2)$ and $Fe(3)$ concentrations are strongly controlled by the pH of the solution. Generally, their solubility increases with a decreasing pH. However, as the increase of their solubilities is not proportional, the

$Fe(2)/Fe(3)$ ratio can change and so does the pe.

3.2.8 Model variants

- To see the effect of calcite buffering rerun the model with a much smaller initial calcite concentration and compare how far the low pH zone and dissolved aluminium are migrating in this case.
- Test the effect of calcite-filled permeable reactive barrier (PRB). To do that add a small zone (between x = 40m and x = 50 m and y = 0m and y = 10m) where a high concentration of calcite is present but no other minerals. After rerunning the model inspect the evolution of the low pH zone and of the aluminium migration.

3.3 PHT3D Exercise 3: Transport and nitrification of ion exchangeable ammonium

This modelling example is based on a field site contamination problem near Mansfield UK (see, e.g., **?????**), where ammonium liquor, a by-product of the production of smokeless fuel, has polluted groundwater over several decades. A reactive transport modelling study that integrated and reproduced the major processes that were believed to occur at the field site was presented by **?**. 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. In the modelling example the development of an ammonium plume and the subsequent flushing of ammonium contaminated groundwater by pristine background water is simulated. The processes included in the example are advection, dispersion, cation exchange and the kinetically controlled oxidation of ammonium. Dispersion, ion exchange and nitrification act as attenuation processes for ammonium.

For simplicity the two-dimensional reactive transport problem is set up for the same model domain as the previous exercise. However, the simulation period is now divided into two different phases. The first phase represents the period of active contamination during which the plume grows successively while the second phase represents the period after the source was exhausted. During this second phase clean groundwater will enter the model domain over the entire depth of the upstream boundary. Furthermore, we also include now the simulation of groundwater recharge in this model.

3.3.1 Modification of the flow problem

For convenience the flow model is similar to the one used in the previous exercise, i.e, the spatial dimensions were modified from the original field setting. The details of the flow model and its discretisation are listed in 3.7. To adapt the MODFLOW model from the previous exercise to the present case, proceed as follows:

- Make a copy of the flow model that was readily prepared for this exercise and save it in a new folder. The model files are located in the folder **2d_flow_problem_haerens**.
- Select Parameters and select the Time button. and change the Total Simulation Time to 3000 days and select a Step Size to 40 days.

Table 3.7: Flow and transport parameters used for PHT3D Exercise 3.

Flow simulation	steady state
Total simulation time (*days*)	3000
Time step size	40
Model length (m)	100
Model thickness (m)	10
Grid spacing Δx (m)	4
Grid spacing Δz (m)	0.5
Porosity	0.35
Horizontal hydraulic conductivity (m)	1 m/d
Vertical hydraulic conductivity (m)	1 m/d
Piezometric head upstream boundary (m)	12 m
Piezometric head downstream boundary (m)	10 m
Longitudinal dispersivity (m)	0.5
Transversal dispersivity (m)	0.05

- To add groundwater recharge we first need to activate the MODFLOW recharge package such that it is availale within iPHT3D. To do this, go to iPHT3D's top menu and select Add-in → Modflow Modules. You will see a list of all available MODFLOW packages and you will see which ones are already activated. Add the recharge package by ticking the box near RCH. Now go to Spatial Attributes → MODFLOW → RCH → rch.2 Recharge Value to specify a rechare rate of 0.001 m/day, i.e., 1 mm per day. Don't forget to press ok once you have entered the value.
- Now rerun MODFLOW to regenerate the flow-file (mt3d.flo), which will later be used by the transport model.

3.3.2 Data input for solute transport properties

For the simulation of the solute transport of the mobile components the model parameters that control advective and dispersive transport need to be entered.

- Go to Parameters → Transport and select the Parameter button
- In the dialog box that subsequently appears, select ADV and select under adv.1 Solver Parameters the 3rd-order TVD Scheme (ULTIMATE) as the Solution Scheme. Leave the default parameters and click OK.

- Select Spatial Attributes → MT3DMS → DSP, enter a longitudinal dispersivity value of 0.5 m. and click OK
- Select Spatial Attributes → MT3DMS → DSP, and specify that the ratio between transverse vertical dispersivity and the longitudinal dispersivity is 0.01. This will define that the actual value is 0.005 m (= 5 mm).
- Make a quick test and assess the conservative transport behaviour in this setting. To do this select Spatial Attributes → MT3DMS → BTN → btn.13 Concentrations and specify a small zone in the upper left corner of the model (near the inflow boundary) for which a concetration of 1 (or any other concentration > 0) is defined.
- Under Parameters → Transport use the Pencil Button to write all the input files required to run MT3DMS
- Under Parameters → Transport use the Red Arrow button to start the MT3DMS simulation
- Inspect the results by navigating in the Results panel of ipht3d. For example to see the concentration contours select Results → and select Tracer. Then select the first timestep under → Tstep and observe the plume spreading by using the right arrow button to move to subsquent timesteps.

3.3.3 Reactive transport

Based on the flow and conservative transport model the next step is to define the input for the reactive transport.

- Copy the database file that will used for this PHT3D exercise into the folder that contains all files for this exercise and make sure its name is **pht3d_datab.dat**. You can use the same dataase as in PHT3D Exercise 1, i.e., the standard PHREEQC database.
- Go to Parameters → Chemistry and select the Import database button. iPHT3D will then read and interpret the PHT3D database file.
- In this next step we define all initial concentrations of all aqueous components and also the two types of water compositions at the upstream model boundary (which will be allocated to the inflowing groundwater). Activate the equilibrium components (tick the checkboxes) that are included and also enter the concentrations

provided in 3.8. Note, that there is no need to include aqueous components that will not play a role in the simulations, such as **Mn(2)**, **Mn(3)** and **Si**. However, consider and activate all valence states of redox-sensitive components. For example, activate all valence states of nitrogen, i.e., **N(5)**, **N(3)**, **N(0)** and **Amm**.

- The composition of the ambient water (initial water composition at the start of the simulation) needs to be entered under the Solutions Tab in the Background column and a second time in the Tab for Solu 2. This solution can also be used to define the recharge water composition. The water composition of the contaminated water will be entered in the Tab for Solu 1. If the concentration of an aqueous component is 0 it is not necessary to enter the value.

- Calcite is the only mineral that is considered in this simulation. It must be activated and the corresponding initial concentrations must be entered under the Phase Tab.

- The allocation of the appropriate water compoitions as model boundary condition can be done by selecting Spatial Attributes → MT3DMS → BTN → btn.12 Boundary Condition and defining a zone (line) for the lower section of the inflow (upstream) boundary (between y = 0m and y = 7m) for which a value of -1 is allocated. This defines that the concentrations at these grid cells will not change during the entire simulation. The concentrations that iPHT3D will allocate to the model's grid cells are the ones defined as initial concentrations. This means that the water composition that was defined as background water composition will at these locations also be used as inflow water composition.

- To additionally define that the two different water compositions that sequentially enter the boundary's upper section we need to select Spatial Attributes → PHT3D → PH → ph.4 Source Sink and define a zone (line) for the uppermost 3 m (y= 7m to y = 10m) of the boundary. In the dialog that comes up with the Zone selection enter two lines under Zone Value. In the first line enter 0 1 and in a separate second line enter 1000 2. This means that $Solution1$ (as defined in the Solutions Tab) will be used until day 1000 and $Solution$ 2 will be used until day 3000.

- To correctly define the recharge water composition select Spatial Attributes → PHT3D → PH → ph.5 Recharge and define a zone (line) across the uppermost layer. In the dialog that comes up

Table 3.8: Concentrations of aqueous components and initial mineral concentration in PHT3D Exercise 3.

	Background and flushing water C_{backgr}, C_{flush} $mol\ l^{-1}$	Contaminated water $C_{cont.}$ $mol\ l^{-1}$
O(0)	2.51×10^{-4}	0
Na	8.62×10^{-4}	1.30×10^{-3}
K	1.24×10^{-4}	1.30×10^{-4}
Ca	1.83×10^{-3}	1.50×10^{-4}
Mg	1.38×10^{-3}	5.00×10^{-5}
Amm	0	6.87×10^{-3}
Cl	1.74×10^{-3}	3.23×10^{-3}
S(6)	9.89×10^{-4}	1.56×10^{-3}
N(5)	8.88×10^{-4}	0
N(3)		0
N(0)	0	0
C(4)	2.82×10^{-3}	2.92×10^{-3}
C(-4)	0	0
pH	7.9	8.3
pe	13.5	0
	C_{init} $mol\ l_b^{-1}$	
Calcite	0.1	

with the Zone selection enter 2 under Zone Value to define that *Solution_2* will be used for recharge.

The pollution source will be active during the first 1000 days, while during the 2000 days following the pollution event the inflowing water is similar to the composition of the ambient water.

3.3.4 Running PHT3D

To run PHT3D, proceed as earlier in the exercise when executing MODFLOW:

- Go to Parameters → Chemistry and use the Pencil Button to write all the input files required to run PHT3D

- Then go to Parameters → Chemistry and use the Plume Button to start PHT3D.
- After the end of the simulation visualise the ammonium plume and check if the simualtion results are plausible.
- Plot also a breakthrough curve (BTC) for the ammonium concentration at x = 50 m and z = 7m. To compare the results with "observed" data go to the main menu (top row) to Add-in → Batch and add the content of the pre-prepared python script:

  ```
  specIn, data  =  self.importTabFile(ex3BTC1.txt)
  tlist  = core.getTlist2()
  iper  =  range(len(tlist))
  species  = ['Amm',' Ca',' K',' Mg',' Na']
  time, conc, labs = core.onPtObs('B0', iper,' Chemistry',' BTC1', species)
  pylab.figure()
  nrows, ncols = 3, 2
  for i, spec in enumerate(species) :
  pylab.subplot(nrows, ncols, i)
  col0  =  specIn.index(spec)
  pylab.plot(data[:, 0], data[:, col0],' o')
  pylab.plot(tlist, conc[:, i])
  pylab.legend([spec])
  pylab.draw()
  ```

  This will show your simulated and the observed data in comparison.

To improve the agreement between observed and simulated data we now consider ion exchange reactions. To include this process in the reation network and to estimate a suitable value for the cation exchange capacity (CEC) of the exchanger sites proceed as follows:

- To add the exchanger species to the reaction network select go to Parameters → Chemistry and acitivate X- under the Exchange Tab. Add a background value of 0.001 as a first estimate for the CEC.
- Now rerun PHT3D.
- Once the model run is complete, reuse the python script to plot again the breakthrough curves (BTCs) for the ammonium, Ca and Na concentrations and repeatedly compare the results with the observed data.

- Continue this manual calibration of the CEC by rerunning the model with successively improved estimates until a good agreement is achieved.

3.4 Surface complexation

Oxides, hydroxides and organic matter carry a surface charge which enables them to sorb ions from solution. The sorption behaviour depends on the type of mineral and crystal morphology as well as the composition and pH of the solution. A potential develops due to the surface charge and therefore, the equation for the Gibbs free energy (ΔG) contains, besides a chemical term, a Coulombic term to account for the work needed to move ions to or from the surface.

It can be shown that for a dissociation reaction (Appelo and Postma, 2005):

$$\log K_{\mathrm{a}} = \log K_{\mathrm{int}} + \frac{zF\psi_0}{RT \ln 10} \tag{3.1}$$

in which K_{a} is the apparent dissociation constant, K_{int} is the intrinsic dissociation constant, z is the charge of the ion, F the Faraday constant (96,485 C/mol), ψ_0 the potential at the surface, R the gas constant (8.314 J/K/mol) and T the absolute temperature.

The intrinsic dissociation constant, K_{int}, applies to the chemical binding of the ion and the surface. The PRHEEQC database contains a compilation by Dzombak and Morel (1990) of laboratory-determined values of intrinsic dissociation constants for hydrous ferric oxide.

The apparent dissociation 'constant' (K_{a}), however, varies with the potential and thus the charge at the surface. In order to calculate the K_{a}, the ψ_0 needs to be known. PHREEQC uses a double-layer model to relate the charge density on the surface (σ_s) with ionic strength (I, equation 2.7) and ψ_0 (**?**).

3.4.1 PHREEQC Exercise 4: calculation of a charged surface composition

This exercise demonstrates the use of the **SURFACE** keyword, which is used in PHREEQC for surface complexation calculations. The input file has already been prepared and is called kd_surf.phrq. The definition of the surface is as follows:

```
SURFACE 1
Hfo_w 2e-4 600 0.088
Hfo_s 5e-6
-equilibrate 1
```

The names Hfo_w and Hfo_s correspond to the names of the master species in the PRHEEQC database that refer to the weak- and the strong surface sites, respectively. The number that follows is the number of surface sites in moles. For the weak sites, the surface area (600 m^2/g) and mass of ferrihydrite (88 mg) are also specified. Unless these values are explicitly typed for Hfo_s as well, they apply to both the weak and the strong sites.

The input file contains BASIC statements that control the output to a text file in spreadsheet format. The distribution coefficient of Zn is calculated for both the weak and the strong sites, as well as an overall distribution coefficient. The file is called kd_surf.prn and can be opened in the Grid tab of PRHEEQC for Windows after the calculation has finished.

What is the value of the overall distribution coefficient for Zn?

Answer: $K_d = \ldots\ldots.$

Test the effect on the K_d of:

- doubling the Zn concentration? Answer: $K_d = \ldots\ldots.$
- doubling the Mg concentration? Answer: $K_d = \ldots\ldots.$
- doubling the amount of ferrihydrite? Answer: $K_d = \ldots\ldots.$
- changing pH from 7 to 5? Answer: $K_d = \ldots\ldots.$

Chapter 4

Modelling kinetically controlled reactions

In the preceding chapters we have only considered equilibrium chemistry, i.e. situations where chemical reactions occur instantaneously. For reactive transport problems the simplifying assumption of instantaneous reactions is warranted as long as the reaction time scale is fast compared to the transport time scale, which is known as the local equilibrium assumption (LEA, e.g., **?**).

For many applications, however, the kinetics of chemical reactions have to be considered. Examples include the (slow) dissolution of sillicate minerals, microbially mediated decay of organic pollutants and the oxidation of reduced mineral substances. The versatility of PHREEQC allows for simultaneous modelling of both equilibrium and kinetic processes, which will be the topic of the present chapter. The PHREEQC cases that will be discussed were taken from **?**.

4.1 Modelling bioremediation processes

In order to be able to design active bioremediation systems and to understand passive bioremediation (natural attenuation), mechanistic descriptions that quantify microbial activity are needed. Since both the rate of microbial growth and the rate of contaminant utilization are highly dependent on the amount of biomass available to catalyze the reactions, such models must have the capability to predict both transient and spatial variations in biomass. To model the production of biomass and the related consumption and production of other chemicals, the key steps are (1) to formulate the rate expressions for the reaction kinetics and (2) to determine the stoichiometry of the biodegradation reactions and, in order to describe the temporal variations.

In the macroscopic mathematical descriptions of microbial growth dynamics aimed at governing laboratory or field scale processes, many of the complex interdependencies that are known at the microscopic scale are commonly neglected and described by empirical formulations based on the classical works of **?** and **?**. The expression describing a specific bacterial growth rate, v_{sp}, observed in many batch experiments is:

$$v_{sp} = v_{max} \frac{C_{org}}{K_{org} + C_{org}} \tag{4.1}$$

where C_{org} is the concentration of the organic substrate, v_{max} is an assymptotic maximum specific uptake rate and K_{org} is the half-saturation constant, which is the substrate concentration at which the actual uptake rate equals $v_{max}/2$. Based on equation 4.1, the total uptake rate v_m considers the dependency of the change of microbial mass on the actual microbial concentration X itself:

$$v_m = v_{max} \frac{C_{org}}{K_{org} + C_{org}} X \tag{4.2}$$

An additional (potential) growth limitation by electron acceptor availability might be incorporated into 4.2, leading to:

$$v_m = v_{max} \frac{C_{org}}{K_{org} + C_{org}} \frac{C_{ea}}{K_{ea} + C_{ea}} X \tag{4.3}$$

where C_{ea} is the electron acceptor concentration and K_{ea} is the appropriate half-saturation constant.

The complete mass balance equation for the microbial mass, X, describing the change of microbial concentration as a function of time, includes both a microbial growth and decay term:

$$\frac{\partial X}{\partial t} = \frac{\partial X_{growth}}{\partial t} + \frac{\partial X_{decay}}{\partial t} \tag{4.4}$$

with

$$\frac{\partial X_{growth}}{\partial t} = Y_x v_{max} \frac{C_{org}}{K_{org} + C_{org}} \frac{C_{ea}}{K_{ea} + C_{ea}} X = Y_x v_m \tag{4.5}$$

in which Y_x is a stoichiometric factor and

$$\frac{\partial X_{decay}}{\partial t} = -v_{dec} X \tag{4.6}$$

where v_{dec} is a decay rate constant.

During growth ($v_m > 0$), both organic substrate and electron acceptors are consumed at rates that are proportional to v_m, which will be illustrated in the following example of toluene degradation under sulfate-reducing conditions.

4.1.1 PHREEQC Example: Kinetic toluene degradation

The stoichiometry of the reactions that describe the microbial degradation of organic compounds depends on the efficiency of the microorganisms to divert electrons (gained in the oxidation step) to either biomass generation or towards electron acceptors. Assuming that 10% of the carbon is incorporated into biomass, the oxidation of toluene under sulfate-reducing conditions can be described by the following overall reaction:

$$\begin{aligned} C_7H_8 + 0.14NH_4^+ + 4.15SO_4^{-2} + 2.58H_2O + 1.86H^+ \rightarrow \\ 6.30HCO_3^- + 0.14C_5H_7O_2N + 4.15H_2S \end{aligned} \tag{4.7}$$

Equation 4.7 shows that the complete mineralization of 1 mol of toluene consumes 4.15 mol of sulfate (during growth) and yields 0.14 mol of sulfate-reducing bacteria (represented by the genralized chemical formula for biomass: $C_5H_7O_2N$). Therefore:

$$\frac{\partial X_{growth}}{\partial t} = 0.14 v_m \tag{4.8}$$

and

$$\frac{\partial C_{sulf}}{\partial t} = -4.15 v_m \tag{4.9}$$

These equations can be implemented in PHREEQC to compute the temporal development of toluene, sulfate and the microbial mass in a batch experiment. Tables 4.1 and 4.2 list the initial conditions and rate constants for the simulation.

The input file toluene_degradation.phrq is available and can be opened in PHREEQC for Windows. Two new aqueous species are defined in the input file that represent toluene (species name: Toluene) and X (species name: Sulfred, since X is already reserved for exchange species).

The rate expressions for toluene degradation and biomass decay are defined under the keyword **RATES**. They are programmed in BASIC, which can be interpreted by PHREEQC so that any type of user-defined rate expression can be modelled.

```
RATES
Toluene_sulf
-start
1 k_Tolu = 1e-05
2 k_Sulf = 1e-05
4 v_up_max = 5.0/86400
10 mTolu = TOT(”Toluene”)
22 mSulf = TOT(”S(6)”)
30 mSulfred = TOT(”Sulfred”)
32 IF (mTolu < 1e-08) THEN GOTO 200
34 IF (mSulf < 1e-09) THEN GOTO 200
40 mon_Tolu = mTolu / (k_Tolu + mTolu)
50 mon_Sulf = mSulf / (k_Sulf + mSulf)
80 growth = v_up_max*mon_Tolu*mon_Sulf*mSulfred
```

Table 4.1: Initial concentration for simulation of a batch experiment of toluene degradation under sulfate-reducing conditions.

Component	Concentration mol/l
Toluene	$1.0 \cdot 10^{-4}$
N	$1.0 \cdot 10^{-4}$
S(6)	$4.5 \cdot 10^{-4}$
Sulfred[1]	$1.0 \cdot 10^{-8}$

[1] Sulfred: sulfate reducing bacteria

Table 4.2: Rate constants for simulation of a batch experiment of toluene degradation under sulfate-reducing conditions.

Component	Constant
K_{sulf} (mol/l)	$1.0 \cdot 10^{-5}$
$K_{toluene}$ (mol/l)	$1.0 \cdot 10^{-5}$
v_{max} (1/day)	5.0
v_{dec} (1/day)	0.1

```
100 rate = growth
110 moles = rate * TIME
200 SAVE moles
-end

Sulfred
-start
10 v_decay = 0.1/86400
15 c_min = 1e-08
20 mSulfred = TOT(”Sulfred”)
30 IF (mSulfred - c_min > 0) THEN inhibit_fac_decay =
(mSulfred - c_init)/mSulfred
35 IF (mSulfred - c_min = 0) THEN inhibit_fac_decay = 0
40 IF (mSulfred - c_min < 0) THEN inhibit_fac_decay = 0
190 rate = v_decay*mSulfred*inhibit_fac_decay
200 moles = rate * TIME
220 SAVE moles
-end
```

Try if you can understand the syntax here. In lines 1, 2 and 4 of the toluene degradation rate block, the constants from table 4.2 are specified. Then, the total concentrations of the aqueous components Toluene, S(6) (sulfate) and sulfate reducing bacteria are read from PHREEQC's internal memory (lines 10, 22 and 30). Then in lines 32 and 34, a check is carried out to make sure that the concentrations of toluene and sulfate are sufficiently high. Otherwise, the rest of the code is skipped, which means that the rate becomes zero. Lines 40, 50 and 80 implement the actual rate expression according to equation 4.5. The number of moles that react are calculated by multiplying the rate times the duration of the time step (the TIME parameter) in line 110 and passed back to PHREEQC in line 200 with the SAVE statement.

The rate expression for the decay of the sulfate reducing bacteria is constructed in a similar way under the identifier Sulfred. Note that an extension of equation 4.6 is used in line 30 to limit the decay rate by multiplying with $(X - X_{init})/X$, where X_{init} is the initial concentration of sulfate reducing bacteria.

The **KINETICS** keyword actually incorporated the rate expressions into the PHREEQC simulation. The names of the rate expressions are listed (Toluene_sulf and Sulfred) and the identifier -steps takes care of the temporal discretization. The -formula identifiers control the stoichiometric proportions of aqueous species which are released or consumed per mole kinetic reactant. In this example, for case a, 0.14 moles of sulfate reducing bacteria are produced for each mole of toluene reacted, which removes 0.14 moles of $C_5H_7O_2N$ from the solution. A negative stoichiometric coefficient indicates that a species is removed from the solution for each mole of kinetic reactant formed, which is why the stoichiometric coefficient for toluene is -1.

The keyword **USER_GRAPH** control the graphical output of this simulation. If you go to the Chart tab in PHREEQC for Windows and start the calculations you can even see the chart being filled with data points during the calculation. The BASIC statements GRAPH_X, GRAPH_Y and GRAPH_SY allocate numbers to the x-, y- and secondary y-axes respectively. The identifiers are basically self-explanatory.

Notice that two cases are considered in this example: case a and case b. Case b differs from case a in that the effects of the different valence state of bacteria (compared to the end-product CO_2) and the related geochemical changes are not considered. All sulfate is consumed during bacterial growth but none during bacterial decay.

Run the model for case a first and look a the chart. Notable is the lag-period of several days before the degradation affects the aqueous concentrations of toluene and sulfate. Its length depends largely on the initial bacterial concentration and on v_{max}, the maximum uptake rate (values given in tables 4.2). The removal of the initial toluene mass (0.1 mmol) is reached after 14 days, at a time when approximately 0.415 mmol of sulfate are depleted. The microbial (net) growth then stops immediately ($v_m = 0$) and the microbial mass is subsequently changing at the rate given by equation 4.6, thereby consuming the remaining 0.35 mmol of sulfate.

You can switch to case b by switching the #-signs in front of the -formula identifier under **KINETICS**. Now all sulfate is consumed during bacterial growth but none during bacterial decay. Run the simulation and observe the resulting chart.

4.1.2 PHREEQC Exercise 5: Kinetic BTEX degradation

Of course, the formulations for microbial growth above apply only to the uptake of a single substrate, whereas contamination often involves numerous (organic) compounds. The (possibly simultaneous) uptake of these substrates can be incorporated into the modeling approach described above. The model of **?** states that the growth of the degrading microbial community is simply the sum of the growth rates arising from degradation of individual organic contaminants:

$$\frac{\partial X}{\partial t} = \left[\left(\sum_{n=1}^{n_{org}} \frac{\partial X_n}{\partial t} \right) - v_{dec} \right] X \qquad (4.10)$$

where, in analogy to equation 4.5, each of the growth terms $\frac{\partial X_n}{\partial t}$ can be derived from:

$$\frac{\partial X_n}{\partial t} = Y_x v_{max}^n \frac{C_{org,n}}{K_{org,n} + C_{org,n}} \frac{C_{ea}}{K_{ea} + C_{ea}} \tag{4.11}$$

The uptake rates v_{max}^n can differ between different substrates. In this way, it is possible to model varying degradation rates of different electron donors. This can be necessary when, for example, benzene degrades more slowly in a BTEX (benzene, toluene, ethylbenzene, xylenes) plume than the other compounds. In this exercise, you will model a case of a simultaneous uptake of BTEX constituents by one microbial group. Different initial amounts of organic compounds are present (Table 4.3) and the initial sulfate mass is increased compared to the first example.

Table 4.3: Initial concentration for simulation of a batch experiment of BTEX degradation.

Component	Concentration mol/l
Benzene	$4.0 \cdot 10^{-4}$
Toluene	$3.0 \cdot 10^{-4}$
Ethylbenzene	$1.0 \cdot 10^{-4}$
Xylene	$2.5 \cdot 10^{-4}$
N	$1.0 \cdot 10^{-4}$
S(6)	$5.0 \cdot 10^{-4}$
Sulfred[1]	$1.0 \cdot 10^{-8}$

[1] Sulfred: sulfate reducing bacteria

Table 4.4: Rate constants for simulation of a batch experiment of BTEX degradation.

Component	Constant
K_{sulf} (mol/l)	$1.0 \cdot 10^{-5}$
$K_{benzene}$ (mol/l)	$1.0 \cdot 10^{-5}$
$K_{toluene}$ (mol/l)	$1.0 \cdot 10^{-5}$
$K_{ethylbenzene}$ (mol/l)	$1.0 \cdot 10^{-5}$
K_{xylene} (mol/l)	$1.0 \cdot 10^{-5}$
$v_{max,sulf,benzene}$ (1/day)	0.1
$v_{max,sulf,toluene}$ (1/day)	5.0
$v_{max,sulf,ethylbenzene}$ (1/day)	0.5
$v_{max,sulf,xylene}$ (1/day)	1.0
v_{dec} (1/d)	0.1

The corresponding reaction equations are, for benzene:

$$C_6H_6 + 0.12NH_4^+ + 3.45SO_4^{-2} + 2.64H_2O + 1.38H^+ \rightarrow \\ 5.4HCO_3^- + 0.12C_5H_7O_2N + 3.45H_2S \qquad (4.12)$$

and for ethylbenzene and xylene(s):

$$C_8H_10 + 0.16NH_4^+ + 4.85SO_4^{-2} + 2.52H_2O + 2.34H^+ \rightarrow \\ 7.2HCO_3^- + 0.16C_5H_7O_2N + 4.85H_2S \qquad (4.13)$$

The PHREEQC input file for this exercise is already prepared and available as btex_degradation.phrq. However, you still need to insert some numbers to make it work. Fill in the parameters from table 4.4 at the appropriate locations (these are marked with #-signs).

Run the file and inspect the change of BTEX with time on the Chart tab. Write down the order in which the 4 different compounds degrade:

1.

2.

3.

4.

The **USER_GRAPH** keyword block is set up in such a way that the concentrations of the individual BTEX compounds are plotted in the chart. Modify it to have the concentrations of the biomass and nitrogen displayed instead.

- Explain the temporal concentration patterns of the biomass and nitrogen.

4.2 PHT3D Exercise 4: Microbially mediated petroleum hydrocarbon degradation under sulfate-reducing conditions

Numerical modelling is widely used to analyse and predict the risk associated with using natural attenuation as a remediation scheme. With few exceptions, most practical model applications to contaminated field sites involve a vertically averaged two-dimensional simulation model. This assumes that vertical concentration gradients over the aquifer depth are negligible. However, as pointed out, for example, by **?**, transversal vertical mixing can be a critical (physical) factor for controlling the length of naturally attenuating contaminant plumes.

Unfortunately, most contaminated sites are not well characterised with respect to the vertical distribution of dissolved contaminants and inorganic groundwater constituents within the aquifer. Therefore the identification and quantification of the vertical mixing process (and how to model it) is generally rather difficult.

The present exercise is loosely based on the field (e.g., **????**) and corresponding modelling studies (e.g., **???**) that provided a detailed investigation on the fate of hydrocarbon compounds at a contaminated

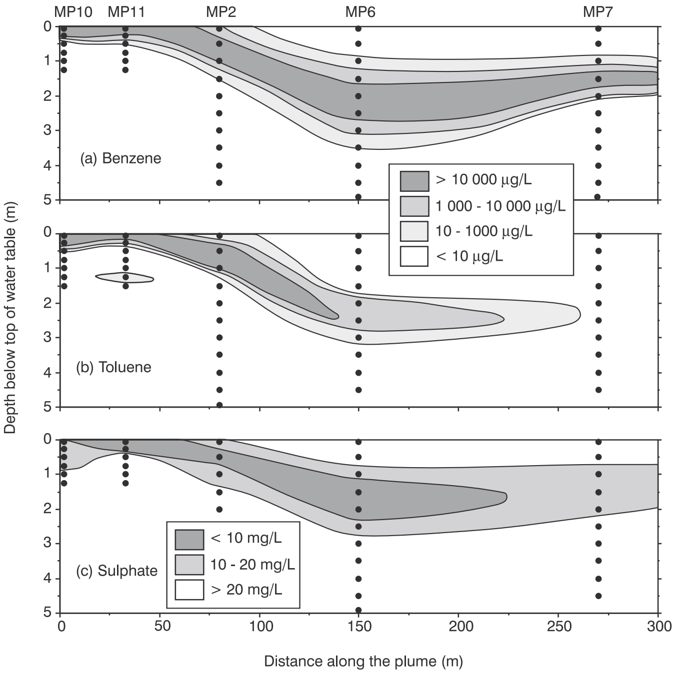


Figure 4.1: Measured benzene, toluene and sulphate concentrations (vertical cross-section) at the Eden Hill field site, after **?**.

site in Perth, Western Australia. At this site detailed information of hydrochemical parameters have been intensively recorded. The data show that toluene, ethylbenzene and xylenes were mineralised under sulfate-reducing conditions in a seasonally varying groundwater flow field while benzene was shown to be persistent. Figure 4.1 shows measured concentrations of benzene, toluene and sulphate for a vertical cross-section along the contaminant plume. The observed long, thin plumes within the relatively homogeneous sand aquifer indicate low transversal dispersivities, providing a significant challenge to achieve an accurate numerical description.

In the exercise you will prepare a simple vertical cross-sectional model along a flow path of the contaminant plume within the unconfined aquifer. The main purpose of the exercise is to demonstrate the

- incorporation of microbial kinetics into reactive transport models
- finge-controlled degradation of contaminant plumes
- simulation of multi-component NAPL (Non Aqueous Phase Liquid) dissolution with the PHREEQC/PHT3D framework and the effect of an ageing NAPL source
- numerical problems that may be associated with advection dominated reactive transport

The exercise has been designed such that all the major phenomena that characterise the behaviour of petroleum hydrocarbon plumes occur within the relatively short simulation period. In reality NAPL concentrations near the water table might be higher and the mixture of compounds within the NAPL phase can also differ from the one used in the present example.

4.2.1 Setting up the flow problem

A cross-sectional model will be set up. Groundwater flow in the model domain is driven by both, inflow from the upstream boundary and by groundwater recharge.

- Set up the model grid using the discretisation suggested in Table 4.5.
- Select Parameters and select the Time button. and set the Total Simulation Time to 600 days and set the Step Size to 5 days.

Table 4.5: Flow and transport parameters used for PHT3D Exercise 4.

Flow simulation	steady state
Total simulation time ($days$)	600
Time step size	5 (d)
Model length (m)	150
Model thickness (m)	4
Aquifer top (m)	20 m
Aquifer bottom (m)	16 m
Grid spacing Δx (m)	5
Grid spacing Δz (m)	0.20
Porosity	0.2
Horizontal hydraulic conductivity (m/day)	20
Vertical hydraulic conductivity (m/day)	20
Flux at upstream boundary (m/day)	0.05
Groundwater recharge (m/day)	0.001
Piezometric head downstream boundary (m)	19 m
Longitudinal dispersivity (m)	0.1
Transversal dispersivity (m)	0.01

- Define a fixed head boundary condition at the downstream end. Consider that such a fixed head boundary condition will not work for grid cells that are positioned above the water table. Therefore make sure that the fixed head condition is only set for the depth zone below 19 m, i.e., for locations below the water table position at the effluent end.

- Allocate suitable initial hydraulic heads.

- Enter a groundwater recharge rate of 0.001 m/day (as descried in the previous example).

- Define a specified flow boundary with a flow rate of 0.05 m/day at the upstream boundary. This can be implemented by adding a well. The required injection rate equals the flow rate multiplied by the height of the aquifer.

- to make sure that the recharge is always applied to the highest active grid cell : Go to Parameters → Flow and select the Parameter button

- In the dialog box that subsequently appears, select RCH and select under rch.1 Flags for recharge the highest active option.

- To prevent drying grid cells activate MODFLOWs (re)wetting capabilities use the same dialog and go to LPF and select under lpf.6 wetting active or inactive the option active under lpf.7 calculation of wetting set the wetting factor **WETFCT** to a value of 0.1 and select the option **h = BOT + WETFCT** × | **THRESH** |. Set the wetting treshold | **TRESH** | to a value of -.01. ???
- Now rerun MODFLOW to regenerate the flow-file (mt3d.flo), which will later be used by the transport model.
- As a check your simulated head at the upstream boundary should be 19.56 m. If your simulated head does not agree with this value revisit the previous steps and try to debug the problem.

4.2.2 Simulating nonreactive transport

Before the reactive transport simulations are started we will briefly check the setup of the model with a tracer transport simulation. Perform the following steps:

- Define the settings for advective and dispersive transport.
- Set the initial concentration (background) to 0.
- Decide what type of boundary conditions would suit the problem.
- Define a contaminant source by defining a concentration value of 1 for the recharge water in the zone between x = 15m and x = 35m.
- Run the simulations and evaluate the plausability of the results.

4.2.3 Simulating the dissolution from a multi-component NAPL source

The first part of the reactive transport simulation considers only the mass transfer process in a NAPL-containing source zone towards the dissolved (i.e., aqueous) phase and the subsequent advective-dispersive transport of the dissolved mass. In the source zone, dissolution of NAPL compounds, (e.g., **?**) acts as a time-varying contamination source for the passing groundwater. The rate at which mass is transferred from the NAPL into the aqueous phase is a function of

- Interfacial area between the NAPL phase and the aqueous phase

- Extent and morphology of the source (in particular the maximum cross-sectional area perpendicular to the main groundwater flow direction)
- Groundwater flow velocity
- Solubility of individual hydrocarbon compounds
- Composition of the NAPL source (mole fraction)

Notwithstanding the relative importance of each of these factors, the concentration of individual hydrocarbon compounds in the groundwater will, at the local scale ((within the contamination source zone, very)) often reach an equilibrium concentration that is equal or close to the multi-component solubility of the compound (**?**). This multi-component solubility $C_{i_{sat},mc}$ is described by Raoult's law (**?**):

$$C_i^{sat,mc} = C_i^{sat}\gamma_i m_i \tag{4.14}$$

where C_i^{sat} is the single-species aqueous-phase solubility (available from tabulated sources, e.g., **?**) of the organic compound in question within a mixture of compounds with different physico-chemical properties, γ_i is the activity coefficient of the i^{th} organic compound (typically assumed to be unity) and m_i is the mole fraction of the i^{th} organic compound within the NAPL mixture. It is defined as

$$m_i = \frac{C_n^i}{C_n^{tot}} \tag{4.15}$$

where C_n^i is the molar concentration of compound i in the NAPL phase and C_n^{tot} is the total molar concentration of all organic compounds in the NAPL phase. A high groundwater flow velocity, among other factors, might result in a kinetically limited dissolution of NAPL compounds. The simplest model that describes the concentration change of the i^{th} compound in groundwater is

$$r_{dis_i} = \omega_i(C_{sat,mc}^i - C_i) \tag{4.16}$$

where C_i is the concentration of the i^{th} organic compound in the groundwater and ω_i is a mass-transfer rate coefficient that is a product of a mass transfer coefficient and the specific interfacial area between NAPL phase and water. The combination of (4.14) and (4.16) applies to arbitrary dissolution rates. Note that ω approaches infinity for equilibrium dissolution. In that case C_i equals $C_i^{sat,mc}$.

For the modelling exercise we use Eqn. (4.16) to compute NAPL dissolution. The equation was translated into a rate expression for the PHREEQC/ PHT3D database. We assume that the NAPL source consists of the four BTEX compounds and that the remaining fraction can be represented by a fifth compound that is assumed insoluble. The computation of benzene dissolution within such a multicomponent NAPL mix can be programmed as follows:

```
Benznapl
-start
# Compute kinetic dissolution from multicomp. NAPL:
10 mBenznapl = tot("Benznapl")
15 if (mBenznapl <= 1e-10) then goto 200
20 solub_Benz = 0.022820
25 mBenz = tot("Benz")
32 mTolunapl = tot("Tolunapl")
34 mEthynapl = tot("Ethynapl")
36 mXylnapl = tot("Xylnapl")
38 mLowsolubnapl = tot("Lowsolubnapl")
40 m_napl_tot = mBenznapl + mTolunapl + mEthynapl
41 m_napl_tot = m_napl_tot + mXylnapl + mLowsolubnapl
42 if (m_napl_tot <= 1e-10) then goto 200
50 msolub_Benz = mBenznapl / m_napl_tot * solub_Benz
60 rate = parm(2) / 24/3600 * (msolub_Benz - mBenz)
70 moles = rate * time
!!! 80 if (moles > m) then moles = m
!!! i suggest to remove that line that slows the computation,
can lead to strange results and is done by default 200 save
moles
-end
```

The above rate expression as well as those for the dissolution of toluene, ethylbenzene and xylene have been included into the database for this exercise. The values used for C_i^{sat} are listed in Table 4.6. Note the much higher solubility of benzene, which is considered the most toxic of the BTEX compounds.

To start the reactive transport modelling

- Copy the file pht3d_datab.ex_eden_hill (which contains the site-specific reaction database) into the model folder and rename it to pht3d_datab.dat
- Import the database and set a very simple water composition that contains only **Na**, **Cl**, **Benz** (= dissolved benzene), **Tolu**

(= dissolved toluene), **Ethy** (= dissolved ethylbenzene) and **Xyl** (= dissolved xylene). Include also the species **Benznapl**, **Tolunapl**, **Ethynapl**, **Xylnapl** and **Lowsolubnapl** which together represent the (immobile) NAPL source.

- For both the ambient water (background) and the recharge water define concentrations of 0.001 mol/l for **Na** and **Cl**, respectively. Set the initial values (initial concentrations) of **pH** to 7 and set the **pe** to 4.0.
- Define a NAPL-polluted source area near the water table (20 m $\geq$ z $\geq$ 19 m) between x = 15m and x = 35m. Select an initial concentration of 0.018 mol/l for the 4 NAPL compounds representing BTEX. Enter an initial concentration of 0.072 mol/l for the compound **Lowsolubnapl** to all the grid cells that sit above a level of 19 m. Note, that the concentration of these immobile NAPL compounds is defined in units of mol/l.
- Define the settings for advective transport: Use the MMOC scheme in this and other PHT3D simulations that include free water tables.
- Define a longitudinal dispersivity of 0.50m and a transverse vertical dispersivity of 5mm.
- Run the simulation and visualise the results.
- Define some observation points and visualise the breakthrough curves of benzene and xylene.
- What explains the different characteristics of the BTCs ?

In the final phase of this exercise we replace the Na-Cl solution with the measured and charge-balanced water composition from the

Table 4.6: Single species solubilities of BTEX compounds used for the simulations in PHT3D Exercise 4.

Aqueous component	C_i^{sat} (mol/l)
Benzene	0.022820
Toluene	0.005978
Ethylbenzene	0.00193
Xylene	0.001800

Eden Hill site as given in **?** and as listed in Table 4.7. The water is anaerobic and only sulphate will act as electron acceptor. As discussed in the earlier PHREEQC example/exercise we will include microbial growth and decay in the simulations. Microbial growth will only occur where both toluene and sulfate are present simultaneously. The rate expression used in the PHREEQC Exercise 5 was slightly modified and compared to Eqn. (4.3) an additional biomass inhibition term was included:

$$v_m = v_{max} I_{bio} \frac{C_{org}}{K_{org} + C_{org}} \frac{C_{ea}}{K_{ea} + C_{ea}} X \tag{4.17}$$

This additional term I_{bio} was introduced to reflect a conceptual model or biologically mediated degradation reactions which suggest that with increasing biomass concentrations and thus increasing biofilm thickness, degradation rates might become limited by the supply of reactants. In order to avoid solving the diffusional transport of reactants at a microscopic (i.e., within biofilm) level, a macroscopic formulation can be used to account for the rate-limitation resulting from excessive biomass accumulation. The biomass inhibition term is computed from

$$I_{bio} = \frac{\theta_{bio,max} - X_{tot}}{\theta_{bio,max}} \tag{4.18}$$

The above equation was used as a base for the computation of the degradation rates with PHREEQC/PHT3D:

```
Tolu
-start
10 mSulfred = tot(”Sulfred”)
20 mSulf = tot(”S(6)”)
30 mTolu = tot(”Tolu”)
35 if (mTolu < 1e-10) then goto 220
40 if (mSulf < 1e-10) then goto 220
68 v_up_max_Tolu = parm(1) / 86400
84 theta_bio_max = parm(2)
90 inhib_bio = (theta_bio_max-mSulfred) / theta_bio_max
95 monSulf = mSulf / (0.0001 + mSulf)
100 monTolu = mTolu / (0.0001 + mTolu)
150 v_up_Tolu = v_up_max_Tolu * monTolu * monSulf
160 v_up_Tolu = v_up_Tolu * inhib_bio
190 rate = v_up_Tolu * mSulfred
200 moles = rate * time
220 SAVE moles
```

```
-end
```

To proceed and include the biodegradation reactions in the simulations:

- Add the additional species to the reaction network.
- Define the background concentrations of the aqueous components and for the recharge water composition according to Table 4.7.
- Enter a value of 1e-07 mol/l as initial concentration for the sulfate reducing bacteria.
- Check if the boundary conditions for the transport are defined correctly such that the inflowing water at the upstream boundary has the same composition as the background and the recharge water.
- Allocate the reaction rate parameters listed in Table 4.8. To enter the values select
- Select Models → PHT3D → Simulation Settings
- Run the model
- Visualise the $microbial\ fringe$.

Table 4.7: Measured and equilibrated aqueous concentrations of the ambient water composition at the Eden Hill field site.

Aqueous component	C_{init}, C_{rech} $(mol\ l_w^{-1})$
pH	5.14
pe	8.01
O(0)	0
N_{tot}	1.00×10^{-4}
C(4)	7.96×10^{-3}
C(-4)	0
S(6)	7.85×10^{-4}
S(-2)	0
Fe(2)	5.20×10^{-5}
Fe(3)	1.46×10^{-5}
Ca	8.42×10^{-4}
K	2.59×10^{-4}
Mg	5.67×10^{-4}
Na	5.25×10^{-3}
Cl	6.46×10^{-3}

Table 4.8: Rate constants for the reactive transport simulation of BTEX degradation under sulfate reducing conditions.

Rate Expression	Parameter Nr	Parameter	Unit	Value
Benz	1	$v_{max,sulf,benzene}$	(1/day)	0.0
Tolu	1	$v_{max,sulf,toluene}$	(1/day)	5.0
Ethy	1	$v_{max,sulf,ethylbenzene}$	(1/day)	2.0
Xyl	1	$v_{max,sulf,xylene}$	(1/day)	2.0
Benz	2	$\theta_{bio,max}$	(mol/l)	$1.0 \cdot 10^{-5}$
Tolu	2	$\theta_{bio,max}$	(mol/l)	$1.0 \cdot 10^{-5}$
Ethy	2	$\theta_{bio,max}$	(mol/l)	$1.0 \cdot 10^{-5}$
Xyl	2	$\theta_{bio,max}$	(mol/l)	$1.0 \cdot 10^{-5}$
Benznapl	1	not used	-	1
Tolunapl	1	not used	-	1
Ethynapl	1	not used	-	1
Xylnapl	1	not used	-	1
Benznapl	2	ω	(1/day)	0.025
Tolunapl	2	ω	(1/day)	0.025
Ethynapl	2	ω	(1/day)	0.025
Xylnapl	2	ω	(1/day)	0.025
Sulfred	1	v_{dec}	(1/day)	0.1
Sulfred	2	C_{init}	(mol/l)	$1.0 \cdot 10^{-7}$

4.3 PHT3D Exercise 5: Pyrite oxidation during deep well injection

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 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 conditions and 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 aluminiumoxides 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. **?** carried out a reactive transport modelling study to analyse 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 seperate aqueous (mobile) component called **Tmp**. The reaction rate expression expression has been programmed such that the value of the component **Tmp** is read and used during the computation of the reaction rate.

4.3.1 Setting up the flow problem

To simplify the original, fully three-dimensional model for this exercise, the flow model is defined as a two-dimensional model for a single stratigraphic layer. Aerobic surface water is injected through an injection well and extracted at an extraction well located 100 away from the injection well.

- Use the data supplied in Table 4.9 to set up the flow model. Note

Table 4.9: Flow and transport parameters used for the deep well injection problem.

Flow simulation	steady state
Total simulation time (*days*)	360
Time steps	180
Model length (column direction) (*m*)	200
Model width (row direction) (*m*)	80
Grid spacing Δx (m)	10
Grid spacing Δy (m)	10
Total Porosity	0.35
Effective Porosity	0.35
Horizontal hydraulic conductivity (*m*)	10
Piezometric head upstream (left) boundary (*m*)	20
Piezometric head downstream (right) boundary (*m*)	20
Depth target aquifer (*m below sealevel*)	between -300 and -310
x-Position injection well (*m*)	145
y-Position injection well (*m*)	5
x-Position recovery well (*m*)	55
y-Position recovery well (*m*)	5
1/2 Flow rate injection well (m^3/day)	500
1/2 Flow rate recovery well (m^3/day)	500
Longitudinal dispersivity (*m*)	1
Transversal dispersivity (*m*)	0.1

that the geometry is defined for a half-model due to the symmetry of the problem. Neglect background groundwater flow and use for simplicity fixed head cells at the left (x = 0 m) and the right (x = 200 m) model boundary to allow exchange of water across these boundaries.

- Check your simulated heads in the injection well (24.22 m) and in the recovery well (15.78 m).

4.3.2 Setting up the nonreactive transport problem

- If the simulated heads agree, use MT3DMS to simulate a simple tracer experiment to estimate the travel times between the injection and the recovery well. Set the tracer concentration in the backgroundwater to 0 and set the tracer concentration in the injection well to 1. Include some observation points on the axis between injection and recovery well to allow the visualisation of breakthrough curves.

- What is your simulated travel time to the mid-point between injection and recovery well ? It should be approximately 20 days. If your result differs, try to debug the problem before proceeding.
- When does the recovery well receive 100% of the injection concentration ?

4.3.3 Setting up the reactive transport problem

Once the tests with the nonreactive model indicate that the model is working properly, proceed with the reactive transport model.

- Add the reaction module (two files) supplied for this exercise to the reaction module library. See the previous exercise for the details.
- Set appropriate boundary conditions for the fluxes/concentrations across the model boundary.
- Copy the reaction database that was developed for this problem into the folder where the iPHT3D model is located.
- Activate the relevant aqueous components that are needed to simulate the reactive transport of the chemicals listed in Table 1 of **?**. Also include **Tmp** (Temperature). For simplicity do not include **DOC** and ion exchange species. From the minerals listed add only **Pyrite (kinetic version)** and **Fe(OH)3(a)** to the reaction network.
- Define the initial concentrations (background water composition and mineral concentrations) in the appropriate iPHT3D Tab. Use the water composition listed in Table 1 of **?**. For pyrite use an initial concentration of 0.05 mol/l bulk volume. Note that the oxidation rate of pyrite is, among other factors, depending on the pyrite concentration. Where pyrite is present at higher concentrations the reaction will proceed faster. For the temperature **Tmp** enter a value of 0.017, which corresponds to 1/1000 of the temperature in Celcius.
- Define the water composition of the injected water as $Solution1$. Use the water composition measured at the 21 January 1997, as listed in Table 1 of **?**. For the temperature add a value of 0.0019

(= 1.9 C). For pe, which is not given in Table 1, use a value of 13.5.

- Attriute this water composition to the injection well under Spatial Attributes → PHT3D → PH → ph.4 Source Sink and define a zone (a single point in this instance) at the well location.
- Make sure that the reaction rate parameters 1 - 5 for the kinetically controlled pyrite oxidation are set to values of 16, .67, 0.5, -.11 and 115, respectively.
- Select the TVD scheme as advection package and define the dispersivities.
- Run the reactive transport model.
- Inspect the results: How far did oxygen penetrate into the aquifer at the end of the simulation time ?

4.3.4 Seasonally changing redox zonation

In the following part of the exercise we attempt to mimic the effects of a seasonally changing injection water temperature. This will result in a dynamically changing redox zonation. To simulate this effect proceed as follows:

- To effectively consider the transiently changing water compositions, iPHT3D allows to upload ascii-files that contain multiple water compositions. For this exercise upload the pre-prepared file that contains the time-varying injectant water compositions. To link the uploaded water compositions to the injection well, modify the previous steady-state input that was made for the Zone that is attributed to the injection well. Go to Spatial Attributes → PHT3D → PH → ph.4 Source Sink, select the Zone and replace the single value with:
  0 1
  30 2
  60 3
  90 4
  120 5
  150 6
  180 7
  210 8
  240 9
  270 10

```
300 11
330 12
```

Note that the heat transport approximation in this exercise is not very accurate as it ignores the retardation that occurs as a result of heat transfer between the injectant and the sediment matrix. While neglected here, it is possible to use MT3DMS/PHT3D to exactly approximate the relevant heat transport equation.

4.3.5 Mobilzation of arsenic

In the last part or the exercise we are going to model the release of arsenic during oxidation of arsenopyrite and its subsequent sorption to ferrihydrite (HfO). In a first step we will model the dissolution of *Arsenopyrite*. The rate expression that is used for *Arsenopyrite* will simply be linked to the rate of the computed pyrite oxidation:

```
##########################
Arsenopyrite
##########################
-start
6 moles = parm(1) * get(1)
200 save moles
-end
```

The stoichiometric ratio at which arsenopyrite will be dissolved, compared to pyrite, is determined by **parm(1)**. For example, if **parm(1)** is set to *0.001* the dissolution of 1 mmol pyrite will be accompanied by the dissolution of 1 μmol *Arsenopyrite*. This is achieved by including **put(1)** in the rate expression for pyrite:

```
##########################
Pyrite
##########################
-start
...
...
...
90 moles = moles_oxy + moles_nitr + moles_0
100 if (moles  m) then moles = m
150 put(moles,1)
200 save moles
```

-end

We do now expand the last simulation and include additionally the two aqueous components As(5) and As(3) as well as the kinetic minerals *Fe(OH)3(a)* and *Arsenopyrite* in the reaction network.

- Set the initial concentration for *Arseonpyrite* to 0.01 mol/l_{bulk}.
- Set the reaction rate constants for *Fe(OH)3(a)* to 2×10^{-13} and define that the ratio of *Arsenopyrite / Pyrite* dissolution is 0.001 (i.e., parm(1) = 0.001 for *Arsenopyrite*).
- Run the simulation and plot a breakthrough curve for As(5) and As(3) at the extraction well and at a location half-way between injection and the extraction well. Save the breakthrough curves from the observation wells to ASCII files.
- Now include surface complexation reactions by copying the file **postfix.phrq** into the folder in which your model is located. This file will be read by PHT3D whenever it is present. In this way some instructions and definitions can be quickly and simply supplied outside the *Visual Modflow* environment. Get the file from the course CD or download it from

  http://www.pht3d.org/course/ex5/postfix.phrq

  Open it with *PHREEQC for Windows* to inspect the input instructions.
- Run the model and inspect again the As(5) and As(3) breakthrough curves at the extraction well (Note, convergence is only achieved if the *diffuse_layer* option is included under the KEYWORD *SURFACE* in the file **postfix.phrq**. As a result the model execution time will increase significantly).
- To compare the new results with the previous results (model run without surface complexation), load the previously saved breakthrough curves (ASCII files) as observations for *As(5)* at the observation wells.

4.4 PHT3D Exercise 6: Degradation of chlorinated ethenes and isotopes

4.4.1 Modelling Scenario

In this exercise we investigate the sequential degradation of chlorinated ethenes and the use of stable isotopes to provide forensic evidence for the origin of elevated vinyl chloride concentrations in a pumping well.

The principle modelling scenario consists of an aquifer that is contaminated by two different contaminant spillages, both positioned below sites of former metal processing companies (Company E and Company W). The modelling scenario is set up for a vertical cross section. The two different contamination sources consist of NAPL pools that are located on top of clay lenses. One of the NAPL sources is assumed to consist of PCE (tetrachlorethylene), while the other is assumed to consist of a mixture of TCE (trichlorethylene) and toluene. Groundwater is entering the model domain through the Eastern (fixed hydraulic head = 13.7 m.a.s.l) and Western boundary (fixed hydraulic head = 14.5 m.a.s.l). Under natural conditions the groundwater discharges to the river (prescribed hydraulic head = 10.8 m.a.s.l). However, there is also an active pumping well located between the PCE source and the river. The majority of the water that enters the model domain through the fixed head boundary discharges to the well during active pumping. However, some groundwater infiltrates to the river. On the other hand, some river water is also drawn towards the pumping well. The model setup is shown in Figure 4.2

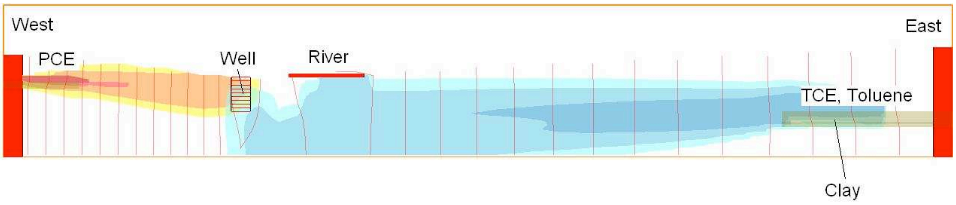


Figure 4.2: PHT3D Exercise 6: Model Setup

4.4.2 NAPL source zones

The contamination sources are modelled by defining two discrete NAPL contaminated zones. On the Western side of the river a PCE source is defined by allocating an initial concentration of 1 mol/l of Pcenapl to a discrete source zone situated on top of the clay lense. Similarly, the

Eastern source is defined by allocating 1 mol/l of Tcenapl and 1 mol/l of Tolunapl to a discrete zone.

The rate expression that controls the kinetically controlled release of PCE is

```
#————————————————————
Pcenapl
#————————————————————
-start
10 mPcenapl = tot(”Pcenapl”)
15 if (mPcenapl <= 1e-10) then goto 200
20 solub_Pce = 1.28 / 131.39 # aqueous solubility of PCE
22 frac_of_solub = parm(2) # Fraction of single species solubility
25 mPce = tot(”Pce_l”) + tot(”Pce_h”)
50 msolub_Pce = frac_of_solub * solub_Pce
60 rate = parm(1) * (msolub_Pce - mPce)
65 if (mPce > msolub_Pce) then rate = 0
70 moles = rate * time
80 if (moles > m) then moles = m
200 save moles
-end
```

In the reaction database similar rate expressions are defined for TCE and toluene.

4.4.3 Formation of dissolved plumes

When groundwater passes through these zones, dissolution (mass transfer to the aqueous phase) will occur, therefore creating a PCE plume on the Western side of the river. On the Eastern side of the river the NAPL source creates a TCE as well as a toluene plume.

During the simulation period of 10 years these plumes grow initially but eventually become stable, given that we assume steady-state flow and constant source release conditions. This means that chemical concentrations at a particular location are not changing any further after a specific simulation time.

4.4.4 Degradation reactions

Besides the plumes of the primary contaminants there are also plumes of the transformation products developing. These result from the degradation reactions that may proceed in suitable hydrochemical and microbial conditions.

Under the oxic conditions found in this river valley aquifer the toluene plume released from the NAPL source undergoes aerobic degradation, thereby consuming oxygen. On the Eastern side of the model domain this creates locally anaerobic conditions between the NAPL source and the groundwater discharge locations.

- Visualise the contours of the toluene plume (Tolu_l) after 10 years (3650 days) simulation time.
- Visualise the oxygen concentration contours after 10 years (3650 days) simulation time.

Where these anaerobic conditions prevail reductive dechlorination of TCE may take place. The transformation follows typically a sequential degradation pathway (TCE → DCE → VC → Ethene). In our model this reaction pathway is incorporated as a sequence of simple first oder reactions. The corresponding reaction rate expression is, for exmaple for TCE:

```
#------------------------------------------
Tce_l
#------------------------------------------
-start
2 if (tot(”O(0)”)) > 1e-7 then goto 60
5 if (tot(”Tce_l”)+tot(”Tce_h”)) < 1e-9 then goto 60
10 rate = parm(1)*(tot(”Tce_l”)+tot(”Tce_h”))
20 ratio = tot(”Tce_l”)/(tot(”Tce_l”)+tot(”Tce_h”))
30 moles = ratio * rate * time
40 put(rate, 3)
50 put(ratio, 4)
60 save moles
-end
```

Note, that the incorporation of an ”if” statement (line 2) inhibits the reaction in the presence of oxygen. The DCE produced in this reaction is subsequently further degraded to VC, the most toxic compound among the chlorinated ethenes. While PCE could be transformed to TCE under reductive conditions, it does not degrade under the aerobic conditions that prevail on the Western side of the mode domain.

4.4.5 Chlorinated ethenes at the pumping well

As a result of the transport and chemical reactions we can find a complex mix of chlorinated ethenes in the pumping well.

- Open the model and inspect the simulation results at the pumping well. Use a particular grid cell that is representing the pumping well (Column 13, Layer 20) for comparison of the results.
- What are the concentrations of Pce_l, Tce_l, Dce_l, Vc_l, and Eth_l ?
- From those concentration alone, is it possible to determine whether the contamination in the well originated from Company E or from Company W ?
- Check the oxygen concentrations at the pumping well (use again the grid cell defined by Column 13, Layer 20). What would this suggest in terms of potential for reductive dechlorination ?

4.4.6 Carbon isotopes

To analyse this modelling scenario further we make now use of the (simulated) carbon isotope ratios. In the model each chlorinated ethene species was divided into two separate species that represent the light and heavy isotopes, respectively. That means that each dissolved compound occurs twice in the reaction database to represent the molecules containing either ^{12}C or ^{13}C. Degradation of the light isotopes typically proceeds faster than the reaction for the heavier isotopes.

The difference between the reaction rates depends on the enrichment factor ϵ. The enrichment factor for a specific reaction may be taken from the literature or, where possible, determined by site-specific experimental work.

The slight difference in reaction rates and the resulting ^{13}C in the mother product is incorporated into the reaction rate expression for the heavier isotope. For example in the case of Tce_h the rate expression is:

```
#----------------------------------
Tce_h
#----------------------------------
-start
2 if (tot(”O(0)”)) > 1e-7 then goto 40
5 if (tot(”Tce_l”)+tot(”Tce_h”)) < 1e-9 then goto 40
10 rate = get(3)
```

```
20 ratio = 1-get(4)
30 moles = ((parm(1)/1000)+1) * ratio * rate * time
40 save moles
-end
```

For each of the chlorinated ethenes the carbon isotope ratios ($^{13}\mathrm{C}/^{12}\mathrm{C}$) can be computed from the simulated concentrations of the light and heavy isotopes. The calculation is done analogous to the calculation of measured concentration values.

The carbon isotope ratio is expressed as permil deviations from the Vienna Pee Dee Belemnite (V-PDB) standard in the conventional notation. For the known, simulated $^{12}TCE_s$ and $^{13}TCE_s$ concentrations the carbon isotope ratio $\delta^{13}C_{TCE}$ can be calculated from:

$$\delta^{13}TCE = \frac{(^{13}TCE/^{12}TCE)_s - (^{13}C/^{12}C)_{Std}}{(^{13}C/^{12}C)_{Std}} \times 1000 \tag{4.19}$$

with

$$(^{13}C/^{12}C)_{Std} = 0.0112372 \tag{4.20}$$

Using these equations, we can now determine the simulated $\delta^{13}C$ values for all chlorinated ethenes.

- Open the spreadsheet **pht3d_exercise_6.xls**
- In iPHT3D extract the select the various species to extract simulated concentrations at specific locations in the model.
- In iPHT3D Extract the simulated concentration values for Pce_l and Pce_h at a location within the Western contaminant source (x = 850 z = 6.5) and near the pumping well.
- Paste the values into the spreadsheet to calculate the $\delta^{13}TCE$ for both locations
- Extract the simulated concentration values for Tce_l and Tce_h at a location within the Eastern contaminant source (x = 70 m, z = 10 m).
- Calculate the $\delta^{13}TCE$ for both locations
- What can be concluded from these values with respect to the most likely origin of the vinyl chloride (VC) ? Has it originated from the site of company W or the site of company E ?

Table 4.10: Compilation of selected model input parameter.

Total simulation time $(days)$	3650
Time step length reactive transport $(days)$	36.5
Groundwater recharge rate (m/day)	0.001
Prescribed heads:	
Western boundary (m)	13.7
Eastern boundary (m)	14.5
River (m)	10.8
Pumping rate (m^3/day)	-7.5
Hydraulic conductivity coarse-grained material (m/day)	40
Hydraulic conductivity clayey material (m/day)	0.1
Longitudinal dispersivity (m)	0.5
Transversal dispersivity (m)	0.005
Source 1:	
$C_{Pcenapl}$ (mol/l)	1
Source 2:	
$C_{Tcenapl}$ (mol/l)	1
$C_{Tolunapl}$ (mol/l)	1
Ambient, recharge and constant head inflow concentrations:	
C_{oxygen} (mol/l)	4×10^{-4}
pH	7
pe	13.5
$C_{Chlorinated\ Ethenes}$ (mol/l)	0
$C_{Toluene}$ (mol/l)	0

Bibliography

Appelo, C. A. J., Postma, D., 1993. Geochemistry, Groundwater and Pollution. A.A. Balkema, Rotterdam.

Appelo, C. A. J., Postma, D., 2005. Geochemistry, Groundwater and Pollution, second edition. A.A. Balkema, Rotterdam.

Barber, C., Davis, G. B., Thierrin, J., Bates, L., Patterson, B. M., Pribac, F., Gibbs, R., Power, T. R., Briegel, D., Lambert, M., Hosking, J., 1991. Final report for project on Assessment of the Impact of Pollutants on Groundwater beneath Urban Areas, July 1989 to June 1991. Tech. rep., CSIRO Division of Water Resources.

Bethke, C. M., 1996. Geochemical reaction modelling. Oxford University Press, Inc., USA.

Broholm, M. M., Jones, I., Torstensson, D., Arvin, E., 1998. Groundwater contamination form a coal carbonization plant. In: Lerner, D. N., Walton, N. R. G. (Eds.), Contaminated land and groundwater: Future directions. Engineering Geology Special Publication. The Geological Society, London, pp. 159–165.

Custodio, E., 1987. Hydrogeochemistry and tracers. Studies and Reports in Hydrology, pp. 213–269.

Davis, G. B., Barber, C., Power, T. R., Thierrin, J., Patterson, B. M., Rayner, J. L., Wu, Q., 1999. The variability and intrinsic remediation of a BTEX plume in anaerobic sulphate-rich groundwater. J. Contam. Hydrol. 36 (3-4), 265–290.

Davison, R. M., 1998. Natural attenuation and risk assesment of groundwater contaminated with ammonium and phenolics. University of Bradford, Bradford, phD thesis.

Davison, R. M., Lerner, D. N., 2000. Proving natural attenuation with modeling at a site contaminated by ammonium and phenolics. In: Sililo, O. (Ed.), Groundwater: Past achievements and future challenges. A. A. Balkema, pp. 737–740.

Eberhardt, C., Grathwohl, P., 2002. Time scales of organic contaminant dissolution from complex source zones: coal tar pools vs. blobs. J. Contam. Hydrol. 59 (1-2), 45–66.

Engesgaard, P., Kipp, K. L., 1992. A Geochemical Transport Model for Redox-Controlled Movement of Mineral Fronts in Groundwater

Flow Systems: A Case of Nitrate Removal by Oxidation of Pyrite. Water Resour. Res. 28 (10), 2829–2843.

Fetter, C. W., 2001. Applied Hydrogeology. Prentice Hall, USA.

Garrels, R. M., Thompson, M. E., 1963. A chemical model for sea water at 25 °C and one atmosphere total pressure. American Journal of Science 260, 57–66.

Grathwohl, P., Klenk, I. D., Eberhardt, C., Maier, U., 2000. Steady state plumes: mechanisms of transverse mixing in aquifers. In: Johnston, C. (Ed.), Contaminated Site Remediation: from source zones to ecosystems, Proc. 2000, CSRC, Melbourne, Vic., 4-8 Dec. 2000. pp. 459–466.

Guerin, M., Zheng, C., 1998. GMT3D - Coupling multicomponent, three-dimensional transport with geochemistry. In: Poeter, E. P., Zheng, C., Hill, M. C. (Eds.), MODFLOW'98. pp. 413–420, Proc. International conference, Colorado School of Mines, Golden, CO.

Haerens, B., 2004. Reactive transport modelling of a groundwater contamination from a former coking plant. Departement of Geografie-Geologie, KU Leuven, Belgium, PhD thesis.

Jones, I., Davison, R. M., Lerner, D. N., 1998. The importance of understanding groundwater flow history in assessing present-day groundwater contamination patterns: a case study. In: Lerner, D. N., Walton, N. R. G. (Eds.), Contaminated land and groundwater: Future directions. Engineering Geology Special Publication. The Geological Society, London, pp. 137–148.

Jones, I., Lerner, D. N., 2001. Natural Attenuation of remnant coking liquor contamination from a deep unsaturated zone. In: Groundwater Quality 2001. Conference pre-prints, Sheffield (UK). pp. 331–334.

Kindred, J. S., Celia, M. A., 1989. Contaminant transport and biodegradation, 2. Conceptual model and test simulation. Water Resour. Res. 25 (6), 1149–1160.

Lichtner, P. C., 1996. Continuum formulation of multicomponent multiphase reactive transport. In: Lichtner, P. C., Steefel, C. I., Oelkers, E. H. (Eds.), Reactive Transport in Porous Media: General Principles and Applications to Geochemical Processes. Mineralogical Society of America, Washington D.C., pp. 1–79.

Michaelis, L., Menten, M. L., 1913. Die Kinetik der Invertinwerkung. Biochemische Zeitschrift 49, 333–369.

Miller, C. T., Poirier-McNeill, M. M., Mayer, A. S., 1990. Dissolution of trapped nonaqueous phase liquids: Mass transfer characteristics. Water Resources Research 26 (11), 2783–2796.

Monod, J., 1949. The growth of bacterial cultures. Ann. Rev. Microb. 3, 371–394.

Noorishad, J., Carnahan, C. L., Benson, L. V., 1987. Development of the Non-Equilibrium Reactive Chemical Transport Code CHMTRNS. Tech. rep., Lawrence Berkeley Laboratory, Earth Science Division.

Parkhurst, D. L., Appelo, C., 1999. User's guide to PHREEQC–A computer program for speciation, reaction-path, 1D-transport, and inverse geochemical calculations. Tech. rep., U.S. Geological Survey Water-Resources Investigations Report, in review.

Plummer, L. N., 1992. Geochemical modeling of water-rock interaction: Past, present, future. A.A. Balkema, pp. 23–33.

Prommer, H., Barry, D. A., 2005. Modeling Bioremediation of Contaminated Groundwater. American Society for Microbiology, pp. 108–138.

Prommer, H., Barry, D. A., Davis, G. B., 1998. The effect of seasonal variability on intrinsic biodegradation of a BTEX plume. In: Herbert, M., Kovar, K. (Eds.), Groundwater Quality: Remediation and Protection. pp. 213–220, Proc. GQ'98 Conf., Tübingen, Germany, 21-25 September 1998, IAHS Public. 250.

Prommer, H., Barry, D. A., Davis, G. B., 2002. Influence of transient groundwater flow on physical and reactive processes during biodegradation of a hydrocarbon plume. J. Contam. Hydrol. 59, 113–131.

Prommer, H., Barry, D. A., Zheng, C., 2003. MODFLOW/MT3DMS-based reactive multi-component transport modelling. Ground Water 42 (2), 247–257.

Prommer, H., Davis, G. B., Barry, D. A., 1999. Geochemical changes during biodegradation of petroleum hydrocarbons: Field investigation and modelling. Org. Geochem. 30 (6), 423–435.

Prommer, H., Stuyfzand, P. J., 2005. Identification of temperature-dependent water quality changes during a deep well injection experiment in a pyritic aquifer. Environmental Science and Technology 39, 2200–2209.

Rubin, J., 1983. Transport of Reacting Solutes in Porous Media: Relation Between Mathematical Nature of Problem Formulation and Chemical Nature of Reactions. Water Resour. Res. 19 (5), 1231–1252.

Schwarzenbach, R. P., Gschwend, P. M., Imboden, D. M., 1994. Environmental Organic Chemistry. John Wiley & Sons, Inc., New York.

Stumm, W., Morgan, J. J., 1981. Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters. John Wiley & Sons, Inc., New York.

Stuyfzand, P. J., 1993. Hydrochemistry and hydrology of the coastal dune area of the western Netherlands. Vrije Universiteit, Amsterdam, The Netherlands, PhD thesis.

Thierrin, J., Davis, G., Barber, C., 1995. A Ground-Water Tracer Test with Deuterated Compounds for Monitoring In Situ Biodegradation and Retardation of Aromatic Hydrocarbons. Ground Water 33 (3), 469–475.

Thierrin, J., Davis, G. B., Barber, C., Power, T. R., Patterson, B. M., Lambert, M., 1992. Groundwater tracer tests within a BTEX contaminated zone in order to determine aquifer parameters and natural degradation rates of organic compounds. Tech. rep., CSIRO Division of Water Resources.

van der Lee, J., de Windt, L., 2001. Present state and future directions of modeling of geochemistry in hydrogeological systems. Journal of contaminant hydrology 47, 265–282.

Walter, A. L., Frind, E. O., Blowes, D. W., Ptacek, C. J., 1994. Modeling of multicomponent reactive transport in groundwater, 1, Model development and evaluation. Water Resour. Res. 30 (11), 3137–3148.

Zheng, C., Wang, P. P., 1999. MT3DMS, A modular three-dimensional multi-species transport model for simulation of advection, dispersion and chemical reactions of contaminants in groundwater systems; documentation and user?s guide. Tech. rep., U.S. Army Engineer Research and Development Center Contract Report SERDP-99-1, Vicksburg, MS.

Acknowledgments

Acknowledgments

Thanks to Bruno Haerens, Janek Greskowiak, Phil Ham, Christopher Schmidt, Boris van Breukelen and many others for their various contributions and for testing the modelling examples.

Appendix I

Options for entering TIC, alkalinity and pH in PHREEQC

There are a number of options available in PHREEQC to enter the carbon concentration, alkalinity and the pH. The best option depends on the problem at hand. The options are:

1. Enter pH and alkalinity. Total moles of carbon(4) is calculated by the program.
2. Enter pH and total carbon. Alkalinity is calculated by the program.
3. Enter alkalinity and total carbon. pH is calculated by the program.
4. Enter pH, estimate of total carbon, and a partial pressure of CO_2. Program will adjust total carbon until desired P_{CO_2} is attained.
5. Enter total alkalinity or total carbon, estimate of pH, and a partial pressure of CO_2. If possible, the program will adjust the pH to attain the desired P_{CO_2}.

The first option is used when both pH and alkalinity were determined in the field. The second option should be used when alkalinity was not titrated in the field but pH and total carbon are known from the laboratory analysis. The third option can be used to check the measured pH of a water sample in which both alkalinity and total carbon were analysed. Options 4 and 5 are useful when the CO_2 pressure of the water sample is known.

Appendix II

Common causes for model crashes

One of the most frustrating things in learning a new code is getting stuck because the model crashes for unclear reasons. Most of the time, the solution is very simple. So simple that overlooking it is easier than finding it. The following checklist may be useful in tracking down the cause of the model failure:

- Model names: Avoid using model names that contain blanks (causes run-time error 53 in PMWIN).
- PMWIN: run-time error 5. This one is a bit of a mystery. Copying the entire folder with the model files to a different folder will probably resolve it.
- Units: Are the values for aqueous concentrations and ion exchanger sites provided in mol/l and in mol/lb for minerals?
- Time stepping: Has the temporal discretization that determines the number of PHREEQC reaction steps been defined? The number of reaction steps should be selected such that solutes are not transported much further than one grid-cell.
- Charge balance of water compositions: Are aqueous solutions that are defined as initial water composition(s) and at model boundaries (recharge, wells, constand head cells, ...) charge balanced?
- Chemical equilibrium of water compositions: Are aqueous solutions that are provided as initial water composition(s) (pre-)equilibrated with the equilibrium minerals that are included in the simulation?
- Chemical equilibrium of water compositions: Are aqueous solutions that are provided as initial water composition(s) (pre-)equilibrated with the ion exchanger sites and have the concentrations on the exchanger been entered?

- Redox: Have all redox-states of redox-sensitive components been included in the definition of the reaction module? For example, for sulphur not only S(6) but both S(6) and S(-2), and/or both C(4) and C(-4), etc?