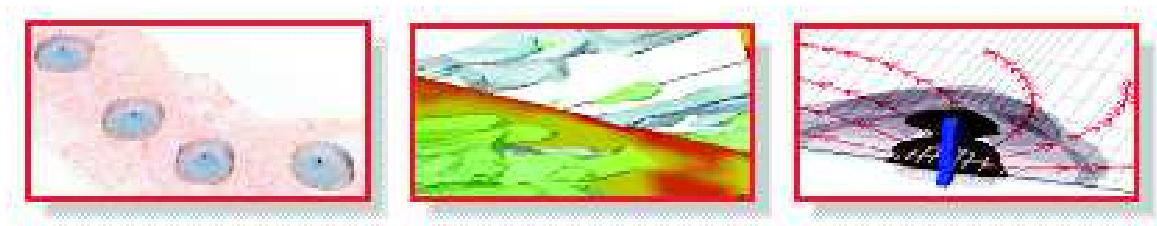


Short Course

Applied Reactive Transport Modelling

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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 water's composition as it travels through the subsurface. Mineral dissolution and precipitation, sorption (transfer of solutes between solution and solids, including ion exchange and surface complexation) and redox processes (reactions that involve transfer of electrons between chemical species) 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

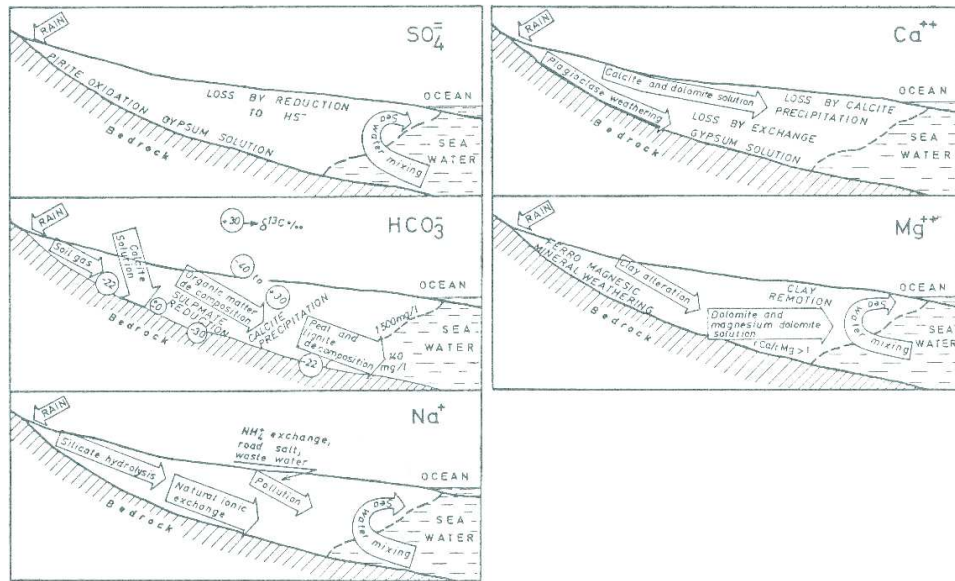


Figure 1: Schematic representation of chemical processes that influence the concentration of major ions in coastal areas (Custodio, 1987).

contained in some silicate minerals that may dissolve but mainly originates 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 (Fetter, 2001) and classification of samples into groups (e.g. Stuyfzand, 1993) 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 Lichtner (1996) 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 (Plummer, 1992). 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 (Lichtner, 1996). Today’s models have reached a level of sophistication that allows us to simulate real-world processes to understand and explain field observations (van der Lee and de Windt, 2001).

Elaborate treatment of the basic concepts and applications of aqueous geochemical modeling can be found in for example Bethke (1996) and Lichtner (1996). This course manual provides a treatment of the basic principles of the models as well as exercises for MT3DMS (Zheng and Wang, 1999), PHREEQC (Parkhurst and Appelo, 1999) and PHT3D (Prommer et al., 2003). 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>
- or PHREEQC-3, which can be obtained for free from the USGS website:
http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/
- ORTI, an open graphical user interface for reactive transport, including MODFLOW, MT3DMS and PHT3D.

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 indispensable 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 2-D Transport Simulation

The main purpose of this first exercise is to learn the use of MODFLOW and MT3DMS for the analysis of a 2-D contaminant transport problem under both natural-gradient and under manipulated hydraulic conditions. The effect of different transport solution techniques on plume migration will be illustrated.

1.1.1 Background: Groundwater Flow

A simple synthetic aquifer system is considered. A sketch of the problem is shown in Figure 1.1. The aquifer is unconfined and drained by a river. We consider that the flow is mainly perpendicular to the river. In the numerical model a fixed head boundary can be assumed for the western boundary of the domain. The southern and northern boundaries can for simplicity be considered as no-flow boundaries assuming that the flow is mainly oriented from the West towards the East. The model domain has an extension of 250 m in East-West direction and 120 m in North-South direction. A hydraulic head of 11 m represents the situation at the western boundary. A fixed hydraulic head of 10.0 m represents the river water level, assuming that the aquifer and the river have a good hydraulic connection. A uniform background horizontal hydraulic conductivity of 10 m/d is assumed. A zone with a slightly higher hydraulic conductivity prevails in a zone of old river channel deposits. A drinking water extraction well is located in the South-East corner of the model domain.

1.1.2 Background: Solute Transport

The contaminant source is represented by a small region in the North-West of the domain. The concentration in the source zone is 10 mg/L throughout the whole zone, as indicated in Figure 1.1. Clean water enters the

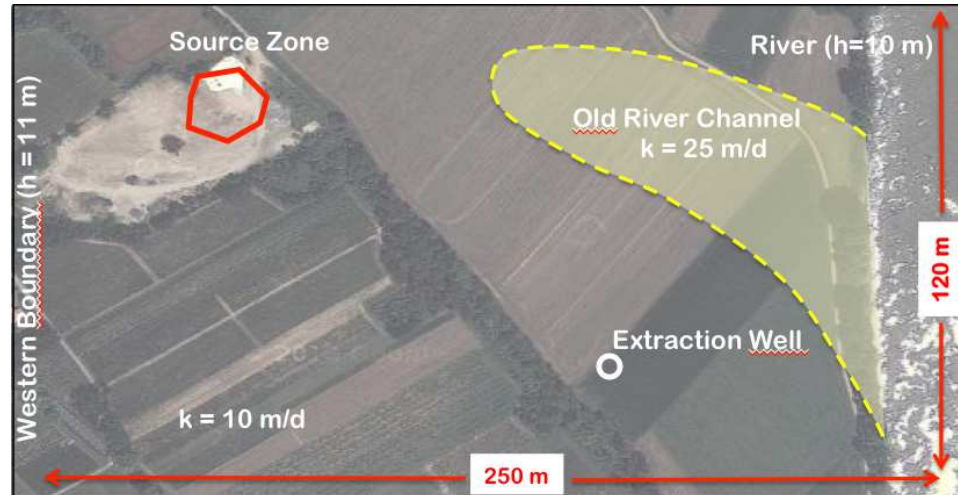


Figure 1.1: Schematic illustration of the contaminated site

upstream boundary, eventually draining to the river under natural flow conditions. The boundary conditions along the northern and southern model boundaries are implicitly defined as zero mass flux conditions. All relevant physical transport parameters are listed in Table 1.1. They are assumed to be uniform throughout the whole model. In the exercise we will use the model to determine the maximum allowable pumping rate in the extraction well such that the contaminant concentrations in that well will remain below $10 \mu\text{g/L}$. We will test various model scenarios and assess the affect of the model discretisation on the model results and of the selection of the solution technique for advective transport.

1.1.3 Setting up the flow model

To set up the flow model proceed as follows:

- In ORTI, create a new model and save it in a new and separate directory (folder).
- Select [Parameters](#) → [1.Model](#) → [Model](#) to specify the model dimension ('2D') and type ('Free')
- Select [Parameters](#) → [1.Model](#) → [Grid](#) to specify the model grid as described in Table 1.1. For the first simulations select a spacing of 5 m in x direction and 2.5 m in y direction
- Set the Top of the aquifer in [Spatial Variables](#) → [MODFLOW](#) → [dis.6](#), and set input for [one_value](#) to 15 m. Do not forget to click on the **OK** button. The bottom is already set to the default value of 0 and does not need to be modified.

- In order to correctly position the spatial objects involved in this model, import a simple map by going to [Parameters](#) → [1.Model](#) → [Map](#). and select the file [mt3dms_ex1.png](#). Note, that only png files can be imported as background maps. The map must have the same size as the domain and will be positioned directly with its corner at the model boundaries. The map can either be active or hidden under the [Results Panel](#) → [1.Model](#) → [Map](#).
- Select [Parameters](#) → [Time](#) → and set the [Total Simulation Time](#) to 800 days. Then define the [Step Size](#) to 25 days. Leave the [Step Mode](#) as Linear.
- Set the boundary conditions for heads by selecting [Spatial Variables](#) → [Modflow](#) → [BAS6](#) → [bas.3 Boundary Conditions](#) by using a (background) IBOUND (Modflow) value of 1 to define active model grid cells. Use the [Zone Tool](#) in the [Add Zone](#) panel to add zones of fixed head BC. For this purpose select the line tool, go into the domain and click the first point around coordinates (0.5, 119) and the second at (0.5, 0.5). This will draw a line at the inflow boundary of the domain. When the second point is selected (clicked), a dialog appears that allows to set the value of the zone. Set the value to -1 (fixed head BC). Leave the value for [Media](#) at the default value of 1 (active grid cell).

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

Parameter	Value
Flow simulation type	steady state
Simulation time (days)	> 800 (until stable)
Model extent column direction (m)	250
Model extent row direction (m)	120
Model thickness (m)	15
Model top elevation (m)	15
Horizontal hydraulic conductivity (background) (m/day)	10
Horizontal hydraulic conductivity (old channel) (m/day)	25
Porosity θ	0.3
Piezometric head upstream boundary (m)	11
Piezometric head downstream boundary (m)	10
Longitudinal dispersivity α_L	1.0 m
Horizontal transverse dispersivity α_{TH}	0.1 m
Effective diffusion coefficient D^*	0

- In the same dialog, create another line to represent the fixed head boundary for the river. For this purpose select the [Polygon Tool](#) and simply click along the river. To end the drawing of the zone right-click on the last point. The value to be entered is again -1.
- To allocate the correct head values at the fixed head boundaries, use [Spatial Variables](#) → [MODFLOW](#) → [BAS6](#) → [bas.5 Initial Heads](#). Define a value of 10 in the dialog box. This value will be used throughout the domain as a starting head for the computations. Note, that this value will not change during the iterations at all location in the model grid for which the boundary was previously defined to be a fixed head boundary condition (i.e., the value was set to -1). In order to specify the fixed head values, draw a line at the same place as the inflow BC and attribute a value of 11 m. As long as the model grid is relatively coarse it is not necessary to put the boundary condition (BC) definition and the heads definition at exactly the same place. However if a more refined grid is used, this will be necessary. In this case it is possible to select one [Zone](#), open the [Zone](#) dialog, and copy the coordinates and reuse/paste them into new [Zone](#) anywhere in the model.
- To define the horizontal hydraulic conductivity value select [Spatial Variables](#) → [MODFLOW](#) → [LPF](#) → [lpf.8 Horizontal Hydraulic Conductivity](#) and set the value to 10 m/d.
- To define the horizontal hydraulic conductivity value in the old river channel zone select [Spatial Variables](#) → [MODFLOW](#) → [LPF](#) → [lpf.8 Horizontal Hydraulic Conductivity](#) and use the [Polygon Tool](#) to define the outline of the zone of higher hydraulic conductivity and set the value to 25 m/d.
- To define a (uniform) porosity value, select [Spatial Variables](#) → [MT3DMS](#) → [btn.11](#) and set the value to 0.3.
- For the initial model runs do not (yet) specify the well.
- Save the model such that your recent changes will not be lost.

1.1.4 Running the flow model

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 [Parameters](#) → [2.Flow](#) → and press the [Write Button](#).
- Select [Parameters](#) → [2.Flow](#) → and press the [Run Button](#).



- ### 1.1.5 Visualising hydraulic heads

- The contours should show a steady-state head distribution similar to that shown in Figure 1.2.

- Set the boundary conditions for concentrations by selecting **Spatial Variables** → **MT3DMS** → **btn.12 Boundary Conditions** (this is the ICBUND value). The value must be equal to 1 (= active cell) throughout the domain. In addition a **Zone** must be created (a polygon) to approximately replicate the source and the value for this **Zone** must be set to -1 to specify a constant concentration boundary condition.

- Define the initial concentrations by selecting [Spatial Variables](#) → [MT3DMS](#) → [btn.13 Concentrations](#). Use the same coordinates as defined previously to allocate an initial concentration of 10 mg/L to this [Zone](#).
- Define the advection package by selecting [Parameters](#) → [3.Transport](#) → [Parameters](#). In the dialog box choose [ADV](#) and [adv.1](#) then [MIX-ELM: Method](#). Select [TVD](#) for the initial transport model runs.
- Define the dispersivity to be used by selecting (in the same dialog), the [DSP](#) → [dsp.2](#) option and enter a value of 1 for the longitudinal dispersivity. Enter also 0.1 for TRPT under [DSP](#) → [dsp.3](#).
- Run the transport model by selecting [Parameters](#) → [3.Transport](#) → and pressing the [Write Button](#). This will write all required [MT3DMS](#) input files. Then press the [Run Button](#) to start the transport simulation.
- A MsDos window will appear and you will see rapidly streaming numbers until the simulation is finished. After the end of the simulation you should see the message *END OF MODEL OUTPUT*.

1.1.7 Breakthrough curves and contour plots

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

- Visualize the concentration contours under [Results](#) → [3.Transport](#) → [Tracer](#). You can change the [Time Step](#) to visualise the results for other simulation times. Also, after selecting a time it is possible to use the mouse wheel to changes times.
- Define an observation well by going to [Spatial Variables](#) → [OBSERVATION](#) → [obs.1 Observations](#) and use the [Zone Tool](#) to draw a point at the desired location.
- Visualise the breakthrough curve by selecting [Results](#) → [5.Observation](#) → [Breakthrough](#), then select the name of the [Observation](#) point you just created. A dialog will appear. Select [Value](#) and the breakthrough curve for this location will appear. The data used for the curve can be exported and used in a spreadsheet or other postprocessing tools.

1.1.8 Impact pumping well on contaminant plume behaviour

- At the location of the well (indicated in the map), add a well in the model by going to [Spatial Variables](#) → [MODFLOW](#) → [wel.1](#) and create a (point) [Zone](#). Select a first estimate for the discharge rate of

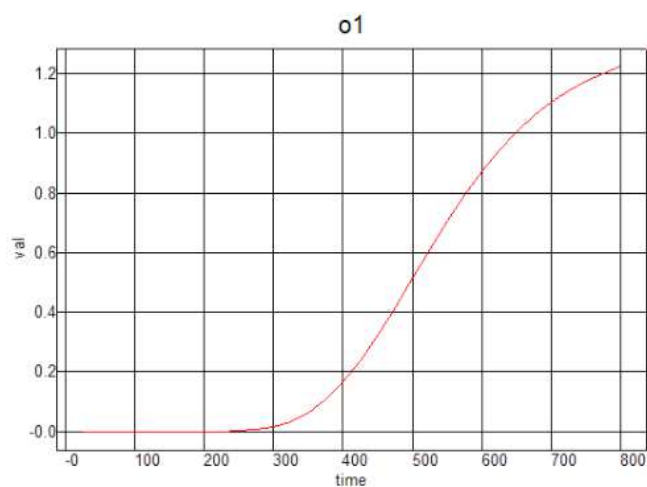


Figure 1.3: Concentration breakthrough curve

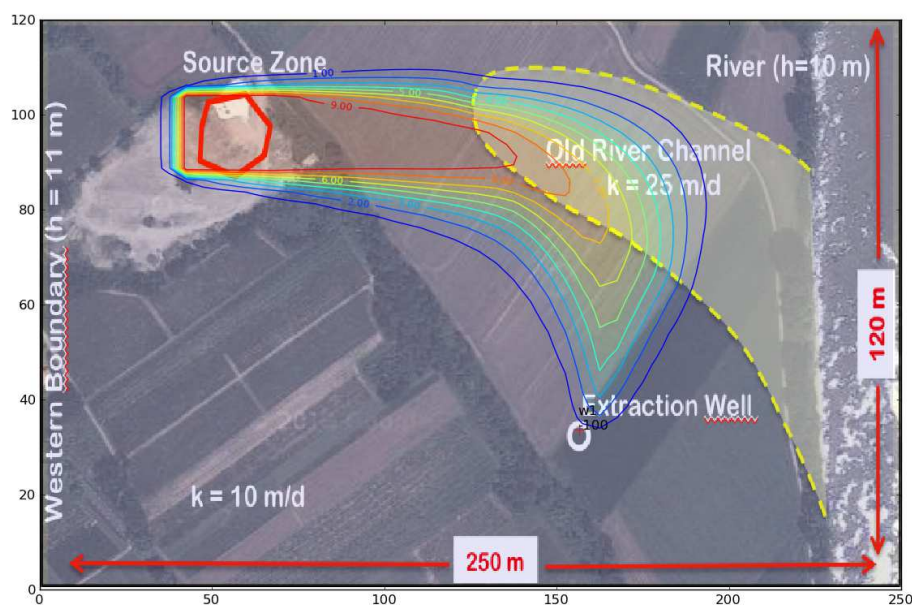


Figure 1.4: Concentration contours after a 800 day simulation time under pumping conditions

the well. Note that negative rates are used for extraction (discharge) and positive values are used for recharge rate. The unit used in this exercise is m^3/d .

- Rewrite the [MODFLOW](#) input files (to do so press the [Write Button](#) and then rerun the flow model).

- Also rewrite the [MT3DMS](#) input files and rerun the transport model.
- To visualise the simulated concentrations at the well an observation point must be set at the location of the extraction well.
- Run the model multiple times to determine the maximum pumping rate for which the contaminant concentration remains under 10µg/L.

1.1.9 Effect of Solution Techniques

Now let us first examine the effect of the employed transport solution technique on the accuracy of simulation results.

- Export the breakthrough curve obtained at the observation point as obtained when using the TVD advection option to an ASCII file.
- Then change the advection solution option to Upstream Finite-Difference, rerun the model and also to MOC, respectively. Export the calculated concentrations to new 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 or other tools to graph the three breakthrough curves.

The TVD and MOC solutions are nearly identical, as both solutions are only minimally affected by numerical dispersion. The Upstream Finite-Difference solution, on the other hand, shows 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 errors, while MOC has a large mass balance error at the beginning. However it should diminish quickly, which is typical for particle-tracking based solution techniques.

1.1.10 Varying the grid resolution

With iPHT3D it is possible to easily vary the model discretisation without the need to change any other model parameters. To test this effect on the breakthrough curve obtained with the Finite-Difference solution technique, go to [Parameters](#) → [1.Model](#) → [Domain](#) and change the grid cell size.

1.1.11 Simulating simple contamination remediation methods

Go back to the case in which no drinking water extraction takes place and use the model to simulate some basic contaminant remediation and/or attenuation scenarios.

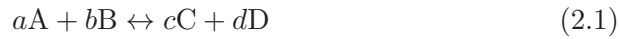
1. **Pump-and-treat:** Illustrate how the contaminant plume could be intersected by adding a pump and treat system at ≥ 80 m downstream of the source zone. Determine the pumping rate that would be required to prevent contaminant discharge to the river. Consider installing multiple wells.
2. **Encapsulate the source zone with a low-permeability barrier:** Illustrate the impact a physical barrier constructed of low-permeability material downstream of the contaminant plume source and/or encapsulate the source zone with low permeability material. Illustrate the impact on both the groundwater flow and on contaminant transport behavior. Experiment with the design of the barrier and create some figures that document the efficiency of your designs on preventing, delaying or minimizing contaminant discharge to the river.
3. **Natural attenuation scenario:** Add a first-order biodegradation reaction as a chemical reaction into the contaminant transport simulation. Determine the first-order reaction rate constant (and the corresponding half-life) that is required such that the contaminant concentration C_{dis} in the groundwater discharging to the river does not exceed $0.001 C_{source}$ (ie the concentration you defined at the contaminant source).

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. Appelo and Postma, 2005; Stumm and Morgan, 1981).

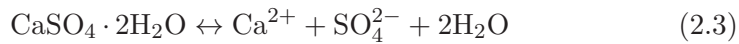
Essential to the description of the equilibrium composition of a geochemical system is the law of mass action. According to this law, the distribution of the species in the reaction:



is given at equilibrium by:

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

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:



The equilibrium constant for this reaction is given by:

$$K_{\text{gyps}} = \frac{[\text{Ca}^{2+}][\text{SO}_4^{2-}][\text{H}_2\text{O}]^2}{[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]} = 10^{-4.60} \quad (2.4)$$

which can be simplified to:

$$K_{\text{gyps}} = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = 10^{-4.60} \quad (2.5)$$

since at low ionic strength (see below) the activity of water $[\text{H}_2\text{O}]$ approaches unity and the activity of a pure solid, $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]$ 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: $K_{\text{gyps}} = 10^{-4.60}$ is valid at 25 °C.

The equilibrium constant is formally dimensionless because the concentration of each species in the expression is divided by 1 in the same concentration units. The entity 1 in the same concentration units is known as the "*Standard State*". The most common standard state used for aqueous species is either 1 mole of the species per litre of solution (1 molar, often abbreviated using an upper case "M" or 1 mole of the species per kilogram water (1 molal, often abbreviated using a lower case "m". The standard state for each aqueous species is incorporated into the equilibrium constant. Thus, although formally dimensionless, the numerical value for the equilibrium is different for different standard states. For example, the numerical value of the equilibrium constant in equation 2.5 where concentrations of Ca^{2+} and SO_4^{2-} are expressed in molar units is different from the value where they are expressed in molal units. In dilute solutions these differences are small compared to analytical errors but at high dissolved salt concentrations differences become significant. In PHREEQC, equilibrium constants in the default database are based on a standard state for aqueous species of 1 mole/kg water. Thus, if we need to solve problems involving concentrated salt solutions where concentrations are expressed in moles/L we will need to consider whether it is appropriate to use the default database. The Standard State situation is more complicated for sorbed species, which will be discussed below.

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 (Appelo and Postma, 2005). 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+} :

$$[\text{Ca}^{2+}] = \gamma_{\text{Ca}^{2+}} \cdot \frac{m_{\text{Ca}^{2+}}}{m_{\text{Ca}^{2+}}^0} = \gamma_{\text{Ca}^{2+}} \cdot m_{\text{Ca}^{2+}} \quad (2.6)$$

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

$$I = 1/2 \sum m_i \cdot z_i^2 \quad (2.7)$$

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

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

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

$$\sum \text{Ca}^{2+} = m_{\text{Ca}^{2+}} + m_{\text{CaOH}^+} + m_{\text{CaCO}_3^0} + m_{\text{CaSO}_4^0} + m_{\text{CaPO}_4^-} + m_{\text{CaF}^+} + \dots \quad (2.9)$$

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 balance 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.

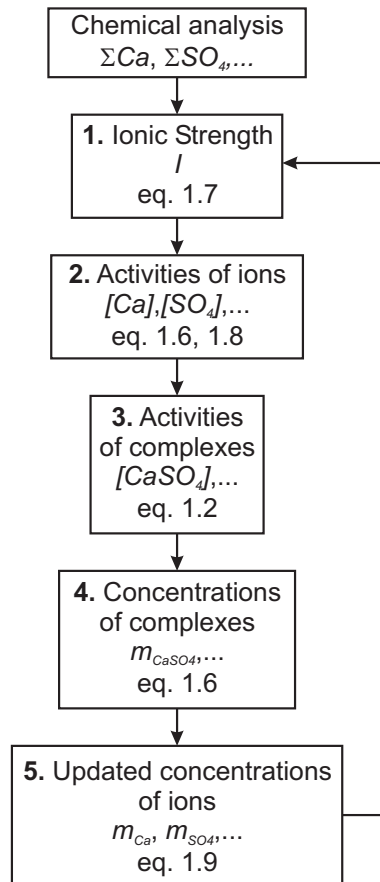


Figure 2.1: Flow chart for speciation calculations (modified from Appelo and Postma, 1993)

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
```

In setting up this example problem we have used "*millimoles*" to express the mass of Ca and F rather than "*milligrams*". Historically, weight-based units of concentration like mg/L were used by geochemists and these are still the concentration units preferred by the regulatory community. So why use "*millimoles*" rather than "*milligrams*" ? One advantage of using millimoles can be illustrated by considering the drinking water limits for arsenic and uranium established by the United States Environmental Protection Agency. The drinking water limit for arsenic is 10 micrograms per liter ($\mu\text{g/L}$) and that for uranium is 30 $\mu\text{g/L}$. These units make it appear as if it takes more uranium than arsenic to contaminate a drinking-water supply. However, if we convert the drinking water limits to moles, we see that the drinking water limit for arsenic and uranium is the same: 0.13 micromoles/L ($\mu\text{moles/L}$). Thus, it takes the same number of arsenic or uranium atoms to contaminate a source of drinking water so that it exceeds the drinking water limit. In chemistry, we are generally concerned with how many atoms or ions there are rather than how much they weigh. This is particularly important when considering reaction stoichiometry. Note that we will need to consider mass when treating isotopic fractionation, which will be discussed later. 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.

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

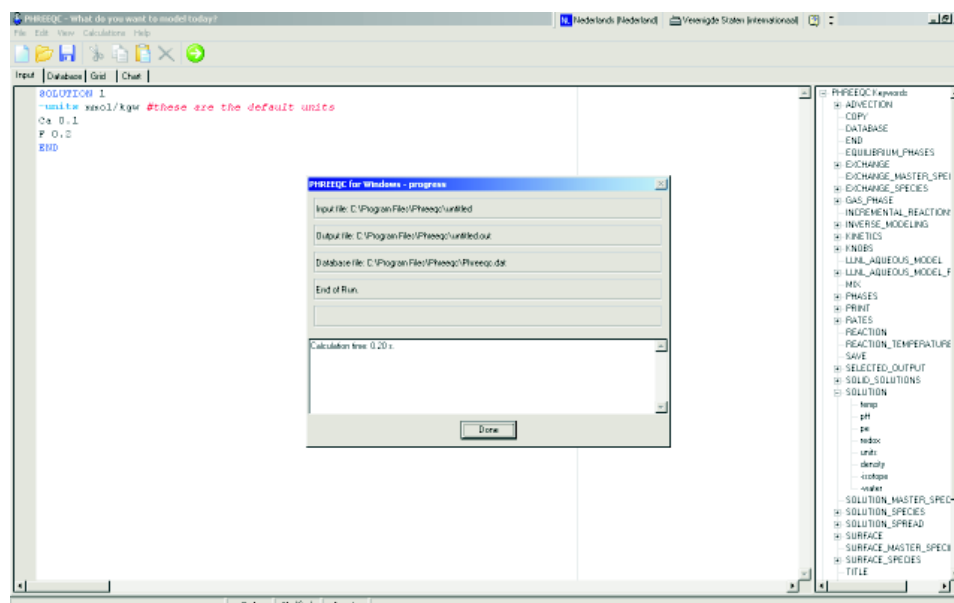


Figure 2.2: Screenshot of the input editor and the progress window after the calculations have finished. The panel to the right of the input editor shows the keywords and identifiers that can be used in PHREEQC.

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: S. Pellegrino mineral water

Since being acquired by the Swiss company Nestle, S. Pellegrino mineral water has become available many places around the world. The S. is presumably an abbreviation for San, since it comes from the San Pellegrino district of Italy. It comes from springs in the Dolomite Mountains of northern Italy. According to the company’s website, hydrogeologic studies have shown that the water originates as snow melt and acquires its composition from interactions with volcanic and carbonate rocks during a 30-year journey underground from recharge to discharge. Carbon dioxide is added during bottling

The PHREEQC input file is given below. Only the pH (= 6.8) has not



Figure 2.3: San Pellegrino mineral water.

been entered yet. Look up the identifier to specify pH and enter it in the input file.

A PHREEQC input file based on the composition of S. Pellegrino water obtained from their website (accessed July 2018) is given below. The reported pH value is 5.7; we will assume it was measured at 25 C. You will need to enter the pH before you can run the simulation.

```
SOLUTION 1 S Pellegrino water composition
-units mg/L
Temperature 25
# Enter the pH on this line
Na 32
K 0
Mg 5.1
Ca 170
Cl 45
Br 0.31
S(6) 390
N(5) 0.71 as N
F 0.48
B 0.14
Alkalinity 170 as CaCO3
END
```

The concentrations here are entered as mg/l. Because PHREEQC recal-

culates all concentrations to moles it is important to specify what molecular weights must be used for recalculating mass-based units (such as mg/l). In this case, alkalinity was reported as CaCO_3 and the statement ‘as CaCO_3 ’ after the concentration ensures that the recalculation is done using the molecular weight of CaCO_3 .

Redox sensitive species can have different valence states. Sulfur in sulfate (SO_4^{-2}) is in the +6 oxidation state and therefore, the name S(6) indicates the sulfate ion. The concentration of nitrate is reported. We designate nitrate, NO_3^- , as N(5) because nitrogen is in the +5 oxidation state.

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 where 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. Is the analysis acceptable on this basis?
- The composition on the website does not report a concentration for silica, Si. How would the calculation of the electrical balance change if we include this element?
- 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: $I = \dots\dots\dots$
- What are the 2 most dominant Ca^{2+} species and their concentrations? Answer:
 1., concentration =,
 2., concentration =
- The website reports a specific conductance of 1200 $\mu\text{S}/\text{cm}$. PHREEQC v.3 will calculate the specific conductance if the Phreeqc.dat (or Amm.dat or Pitzer.dat) database is used. The calculated specific conductance is ???. Is this within 10 % of the reported specific conductance?

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):

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

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:

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

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. $SI_{\text{gyps}} > 0$).

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 Garrels and Thompson (1963) 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 Garrels and Thompson (1963) 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 (Parkhurst and Appelo, 1999):

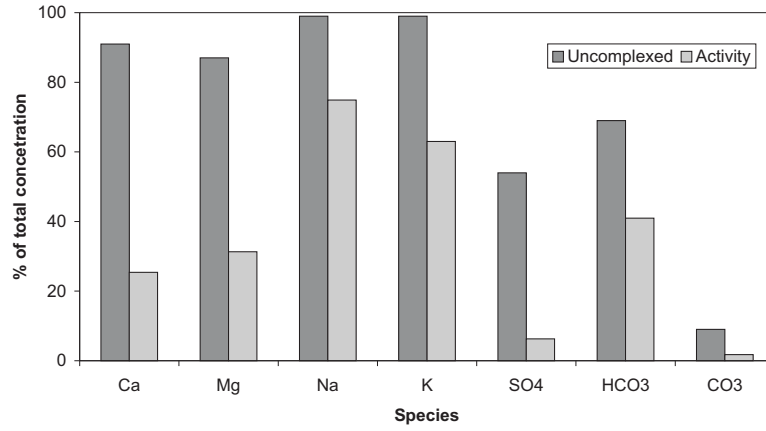


Figure 2.4: Effect of complexation and electrostatic shielding expressed as percentage of total concentration. Based on calculations by Garrels and Thompson (1963).

```

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 free concentrations of Ca^{2+} and CO_3^{2-} amount to $m_{\text{Ca}^{2+}} = 9.504 \cdot 10^{-3}$ and $m_{\text{CO}_3^{2-}} = 3.826 \cdot 10^{-5}$ mol/kgw, respectively. The corresponding activities are $[\text{Ca}^{2+}] = 2.380 \cdot 10^{-3}$ and $[\text{CO}_3^{2-}] = 7.969 \cdot 10^{-6}$ mol/kgw, respectively. Inserting the activities in the expression for the saturation index (equation 2.11) yields:

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

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 $SI_{\text{calcite}} = 2.04$, 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.

- Calculate the saturation index (SI) of the water samples in table 2.1 for fluorite ($\text{CaF}_2 \leftrightarrow \text{Ca}^{2+} + 2\text{F}^-$, $K_{\text{fluorite}} = 10^{-10.6}$), without making corrections for the ionic strength and complexes.

Results:

$$SI_{\text{fluorite},A} = \dots\dots, SI_{\text{fluorite},B} = \dots\dots, SI_{\text{fluorite},C} = \dots\dots$$

- 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:

$$SI_{\text{fluorite},A} = \dots\dots, SI_{\text{fluorite},B} = \dots\dots, SI_{\text{fluorite},C} = \dots\dots$$

- 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:

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

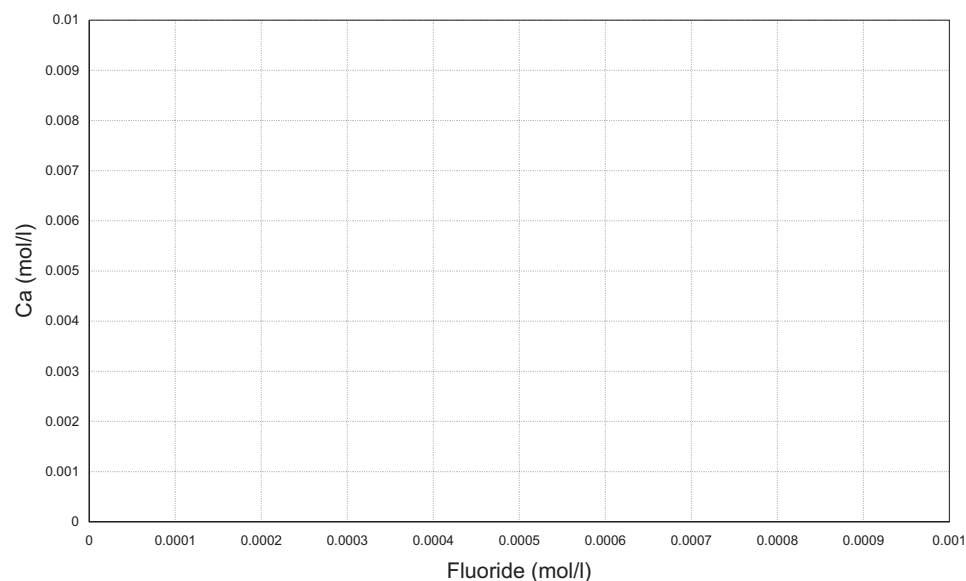


Figure 2.5: Plot of Calcium vs. Fluoride concentrations.

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)

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

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 Engesgaard and Kipp (1992) for a model verification of their MST1D code against the CHEMTRNS model by Noorishad et al. (1987). 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 Engesgaard and Kipp (1992), 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 0.24 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 Engesgaard and Kipp (1992)) 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 ORTI proceed as follows:

- In ORTI, 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 0.24 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 (<i>days</i>)	0.24
Time step (<i>days</i>)	0.01
Grid spacing (<i>m</i>)	0.01
Model length (<i>m</i>)	0.50
Pore velocity (<i>m/day</i>)	0.81
Hydraulic conductivity (<i>m/day</i>)	1
Effective Porosity (—)	0.32
Total Porosity (—)	0.32
Dispersivity (<i>m</i>)	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 $0.259\text{ m}^3/\text{day}$.

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 [Write 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 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 .

3.1.4 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. ORTI 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 ORTI 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.

3.1.5 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 ORTI into the basic transport package file, which is called **pht3dbtn.dat** in PHT3D. The initial concentrations that need to be entered into ORTI, as defined in the paper by Engesgaard and Kipp (1992), 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., $\text{mol l}_{\text{volume}}^{-1}$.

Engesgaard and Kipp (1992) defined their mineral concentrations as mass per mass of soil, i.e., $\text{mol kg}_{\text{soil}}^{-1}$ and provided the bulk density (1800 kg m^{-3}) of the soil. Therefore, their initial concentrations for calcite of $2.176 \times 10^{-5} \text{ mol kg}_{\text{soil}}^{-1}$ translates to $3.906 \times 10^{-5} \text{ mol l}_{\text{volume}}^{-1}$, 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 ORTI.

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}

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 ORTI 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 that contains the input values for the saturation index (SI) and the initial concentration (Backgr_SI and Backgr_Mol, respectively). 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) in the same zone as the well at 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.

3.1.6 Running PHT3D

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

- Go to [Parameters](#) → [Chemistry](#) and use the [Write Button](#) to write all the input files required to run PHT3D

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 ($\text{CaMg}(\text{CO}_3)_2$)	0.0

- 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 *line1*. 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 [0.24](#) 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 *line1*, 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. If you export *Ca*, *Mg*, *Cl*, *Calcite* and *Dolomite* you can copy/paste the results into the pre-prepared excel file and compare your model results with those obtained by Engesgaard and Kipp (1992)

3.1.8 Comparison of simulation results

If all steps of the model definition were performed correctly the results should agree closely with those obtained by Engesgaard and Kipp (1992), 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.

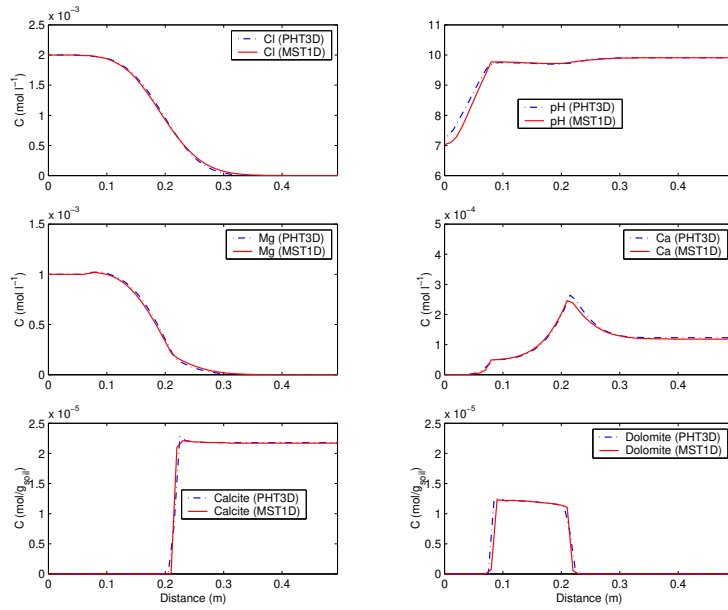


Figure 3.1: Simulation results for PHT3D and MST1D: Aqueous and mineral concentrations after 21000 s.

3.2 PHT3D Exercise 2: Acid rain and mineral buffering

This exercise is a simple two-dimensional simulation problem that involves mineral dissolution reactions. Most importantly this example illustrates the concept of mineral buffering reactions that can occur in response to acidic groundwater recharge entering an aquifer. The problem is set up as a vertical transect representing a small catchment with groundwater being the only driver for groundwater flow. We will study the evolution of the water quality that discharges to the river over a 50-year period (18250 days). This will mimic, although in a crude way, the response to the atmospheric sulfur deposition that has occurred (and in some places still occurs) in conjunction with air pollution from industrial emissions. The increased sulphur input was associated with a decline of the pH within the rain and the recharge water. The increased acidity of the recharge water can cause the enhanced dissolution of selected minerals, which act as pH buffers. The dissolution of these minerals will raise the pH of the groundwater until they are depleted. With the exercise we compare different scenarios and show the influence of the initial concentration of the buffering mineral on the longevity of the buffering process.

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 Table 3.4. To construct the MODFLOW model that underlies the transport problem proceed as follows:

- In ORTI, create a new model and save it 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](#), [free](#) for [Type](#) and [MODFLOW series](#) 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 2000m long and 20m thick. The model domain may be discretised into grid cells of 40m length and 1m height. Note, that the model discretisation can be easily changed again later.
- Select [Parameters](#) and select the [Time](#) button. Set the [Total Simulation Time](#) to 18250 days and select a time [Step size](#) of 182.5 days.
- Go to [Spatial Attributes](#) → [MODFLOW](#) → [LPF](#) → [lpf.8](#) to specify the horizontal hydraulic conductivity to 20 *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 0.25.
- Implement a hydraulic boundary condition that represents the river at the down stream end of this synthetic catchment by defining a specified head boundary at the downstream side 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 draw a short line near the effluent end. Choose an elevation of $z = 8.5$ m for the line and draw it from $x = 1$ m to $x = 20$ m. The value for the line (=zone) needs to be set to -1. Use, for example, *river_bc* as [Zone Names](#). You will see the selected name displayed near the location of the line.

By setting the boundary condition type to -1 the hydraulic head at the grid cells near the defined line will remain unchanged over the entire simulation period, i.e., it will remain at the value that corresponds to the elevation of the river water level. In the next step the initial heads need to be defined.

- First the define the global initial hydraulic head for the entire domain (Background value) by going to [Spatial Attributes](#) → [MODFLOW](#) → [BAS6](#) → [bas.6 Initial Heads](#) and set the [Backg.](#) value to 20m. Then press 'OK' to confirm the value.
- Define the initial hydraulic head at the location of the river by going to [Spatial Attributes](#) → [MODFLOW](#) → [BAS6](#) → [bas.6 Initial Heads](#). Select [Zone](#) and use the [Zone Tools](#) to draw again a short line near the effluent end. Choose an elevation of $z = 8.5$ m for the line and draw it from $x = 1$ m to $x = 20$ m. Note, that you can edit the coordinates manually after you have completed the drawing. The value for the line (=zone) needs to be set to 8.5. Use, for example, *river_head* as [Zone Names](#). You will see the selected name and the selected value displayed near the location of the line.

To define the groundwater recharge for this model you will first need to activate the recharge package, as it is not automatically activated. This can be done by going to [Add-in](#) → [MODFLOW modules](#) and ticking the box [RCH](#). Then tick [OK](#). You will see that you can now go to [Spatial Attributes](#) → [MODFLOW](#) → [RCH](#) → [rch.2 Recharge value](#) and set the [Backg.](#) value to 0.001m, corresponding to an annual groundwater recharge of 365mm per year. Then press 'OK' to confirm the value.

Table 3.4: Flow and transport parameters for the simulation.

Flow simulation	steady state
Total simulation period (<i>days</i>)	18250
Time step length (<i>days</i>)	182.5
Model length (<i>m</i>)	2000
Model thickness (<i>m</i>)	20
Grid spacing Δx (<i>m</i>)	40
Grid spacing Δz (<i>m</i>)	1
Porosity	0.25
Horizontal hydraulic conductivity (<i>m/day</i>)	20
Vertical hydraulic conductivity (<i>m/day</i>)	1
Piezometric head downstream boundary (River) (<i>m</i>)	8.5
Longitudinal dispersivity (<i>m</i>)	2.5
Transverse vertical dispersivity (<i>m</i>)	0.025

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 [Write 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.
- Try, for example to set the head contours manually at 0.25m intervals, starting from 8.5m.

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 [MMOC](#) as the Solution Scheme. Leave the default parameters and click [ok](#).

Table 3.5: Aqueous concentrations used in acid groundwater recharge exercise

Aqueous component	C_{init} ($mol\ l_w^{-1}$)	$C_{recharge}$ ($mol\ l_w^{-1}$)
pH	7.00	4.18
pe	4.00	4.00
Al	1.538×10^{-5}	0
C(4)	6.041×10^{-5}	5.736×10^{-5}
C(-4)	0	0
Cl	9.345×10^{-4}	7.335×10^{-5}
Na	1.000×10^{-3}	2.827×10^{-5}
S(6)	1.000×10^{-6}	1.072×10^{-5}
S(-2)	0	0
Si	1.107×10^{-4}	0

- Select [Spatial Attributes](#) → [MT3DMS](#) → [DSP](#), enter a longitudinal dispersivity value of 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 0.05 m (= 50mm).

3.2.4 Data input for reactive transport

In the following step we will now activate the geochemical reaction network and define the various water and mineral compositions that will play a role in this simulation problem. The initial and the groundwater recharge water composition that will be employed in this example are shown in Table 3.5.

- 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 standard PHREEQC database for this example.
- Go to [Parameters](#) → [Chemistry](#) and select the [Import database](#) button. ORTI will then read and interpret the PHT3D database file.
- In this next step we define all initial concentrations of all aqueous components also the concentrations of the acidic groundwater recharge. 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 , Al , $C(4)$, $C(-4)$, Cl , Na , $O(0)$, $S(6)$, $S(-2)$, and Si and enter the concentrations that are provided in the Table. In the next step define the acid recharge water composition by entering the values from the Table in the [Solution 1](#) column under the [Solutions](#) Tab.

- The [Background](#) water composition will automatically be used to define the initial concentrations.
- The allocation of [Solution 1](#) groundwater water recharge composition can be done by selecting [Spatial Attributes](#) → [PHT3D](#) → [ph.5Recharge](#) and set [Backg.](#) to 1.

3.2.5 Running PHT3D

In this first step we will now run PHT3D without invoking any mineral reactions. This means that all temporal and spatial concentration changes of the aqueous components that occur over the simulation period are solely a function of advective-dispersive transport. This provides the basis for subsequently studying the impact of mineral reactions.

- Go to [Parameters](#) → [Chemistry](#) and use the [Write 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 ORTI. Select a specific timestep and a species for which you want to see your results. For example to see the pH contours after 10 years select [Results](#) → [Aquifer](#) → [Tstep](#) and select [3650](#) 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 breakthrough curves at the river discharge point to illustrate how the quality of the water discharging from the groundwater to the river changes 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 want 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.

- Alternatively you can visualise results with PHT3DPlot.
- What changes occur to the chloride concentrations and what does this mean ?
- How much does pH decrease over the duration of the simulation ?
- Save the simulated breakthrough curves for pH, Si and Al so you can later directly plot and compare these results together with the results from your next model variants.

3.2.7 Role of mineral reactions

- Let's first study the effect of including *Quartz* in this simulation. This can be done under the [Phase](#) Tab. The input allows to activate mineral phases and to define values for the saturation index (SI) to which the mineral should be equilibrated (typically 0). and the initial concentration (Backgr_SI and Backgr_Mol, respectively. Leave the Backgr_SI at the default value of 0 and define a background concentration Backgr_Mol of 1 mol/L_bulk.
- Now rerun PHT3D and inspect again the breakthrough curves for pH, Si and Al.
- How can you interpret these results ?

Now we will inspect the impact of $Al(OH)_3$ on the composition of the discharging groundwater.

- Add initially a relatively small initial concentration such as 1×10^{-4} mol/L_bulk of $Al(OH)_3$, rerun the model and save again the breakthrough concentrations that you obtained for the observation point at the river.
- Increase the initial concentration to a value such as 1×10^{-2} mol/L_bulk of $Al(OH)_3$, rerun the model and save again the breakthrough concentrations that you obtained for the observation point at the river.
- Make comparative plots for pH and Al for your different model variants.

3.3 PHT3D Exercise 3: Precipitation/dissolution fronts in acid mine drainage

This exercise is another simulation problem that involves mineral dissolution and precipitation reactions as the principle geochemical reactions. Compared to the previous exercise it is somewhat more complicated as it contains significantly more aqueous components and mineral reactions. It was first presented by Walter et al. (1994) and later also used as a benchmark problem by Guerin and Zheng (1998). 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 Walter et al. (1994) is used, the simulation includes 17 aqueous components, 15 of which are transported, 54 aqueous species and six minerals.

3.3.1 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 3.6. To construct the MODFLOW model that underlies the transport problem proceed as follows:

- In ORTI, 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 height. 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 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.

3.3.2 Running MODFLOW

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

- Under [Parameters](#) → [Flow](#) use the [Write 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.

3.3.3 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.

Table 3.6: Flow and transport parameters for the simulation.

Flow simulation	steady state
Total simulation period (<i>days</i>)	2000
Model length (<i>m</i>)	100
Model thickness (<i>m</i>)	10
Grid spacing Δx (<i>m</i>)	4
Grid spacing Δz (<i>m</i>)	1
Porosity	0.35
Horizontal hydraulic conductivity (<i>m/day</i>)	1
Vertical hydraulic conductivity (<i>m/day</i>)	1
Piezometric head upstream boundary (<i>m</i>)	12
Piezometric head downstream boundary (<i>m</i>)	10
Longitudinal dispersivity (<i>m</i>)	2.5
Transverse vertical dispersivity (<i>m</i>)	0.025

- 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).

3.3.4 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 the aqueous components that will be used in the simulation are shown in Table 3.7. Also the initial concentrations of the minerals are given in Table 3.8.

- 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 database as in PHT3D Exercise 1, i.e., the standard PHREEQC database.

Table 3.7: 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 3.8: 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 ($CaSO_4 \cdot 2H_2O$)	0.0
amorphous SiO_2	4.07×10^{-1}

- Go to [Parameters](#) → [Chemistry](#) and select the [Import database](#) button. ORTI 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 $y = 0\text{m}$ and $y = 7\text{m}$) 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 ORTI 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 ($y = 7\text{m}$ to $y = 10\text{m}$) 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.

3.3.5 Running PHT3D

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

- Go to [Parameters](#) → [Chemistry](#) and use the [Write Button](#) to write all the input files required to run PHT3D
- Then go to [Parameters](#) → [Chemistry](#) and use the [Plume Button](#) to start PHT3D.

3.3.6 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 ORTI. 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 want 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.

3.3.7 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 Walter et al. (1994). 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 ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) 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 ($\text{Al}(\text{OH})_3$) precipitation is the buffer 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*.

3.3.8 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 $x = 40\text{m}$ and $x = 50\text{ m}$ and $y = 0\text{m}$ and $y = 10\text{m}$) 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.

Chapter 4

Cation exchange

4.1 Background

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

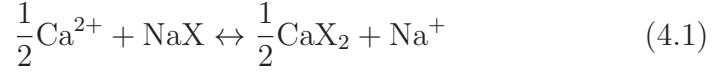
When dealing with sorption processes a distinction is often made between surfaces with a constant exchange capacity (ion exchange) and surfaces with a variable charge (surface complexation). In ion exchange problems, ions are adsorbed and released in equivalent proportions. The exchange capacity of the exchanging surface is assumed constant and the net charge of the surface does not change during the exchange process. This approach works especially well for cation exchange on clay and organic surfaces. In surface complexation, on the other hand, the charge of the surface is variable and dependent on the amount and kind of ions sorbed. It applies for example to sorption of heavy metals on the surface of oxides and hydroxides.

PHREEQC can simulate sorption through ion exchange and surface complexation and both approaches will be discussed below.

Cations readily adsorb to negatively charged clay and organic particles. A change of the composition of the water that is in contact with the exchange complex induces exchange and hence a change in the composition of both the water and the exchange complex. Since the amounts of adsorbed ions can be large compared to the amounts in solution, the effect of this process on the water composition can be significant.

Cation exchange occurs in a variety of natural systems but is especially relevant in coastal areas. In seawater Na, Mg and K are present at increased levels compared to fresh water, which generally contains

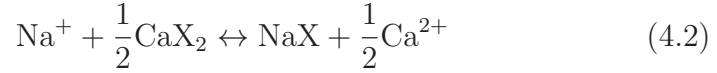
Ca as the dominant cation. When the fresh water displaces the seawater Na, Mg and K from the sediment's exchange complex are displaced by Ca. The exchange of Na^+ (on the exchange complex) for Ca^{2+} that occurs in a freshening aquifer is described by the following equilibrium reaction:



where X indicates the soil exchanger.

As the affinity of the exchanger differs for each individual cation, a spatial separation of the displaced cations can develop. Going upstream of the fresh- saltwater interface a so-called chromatographic sequence of Na, K, Mg and Ca dominated water types is found (Appelo and Postma, 1994).

The reverse occurs when seawater intrudes in a fresh water aquifer:



The equilibrium constant for this reaction is given by:

$$K_{\text{Na}\backslash\text{Ca}} = \frac{[\beta_{\text{Na}}][\text{Ca}^{2+}]^{\frac{1}{2}}}{[\beta_{\text{Ca}}]^{\frac{1}{2}}[\text{Na}^+]} = 0.398 \quad (4.3)$$

where $[\beta]$ indicates the activity of the sorbed species and the subscripts Na and Ca denote the sorbed species NaX and CaX_2 , respectively. The equilibrium constant for cation exchange reactions is also called the selectivity coefficient. Values of selectivity coefficients for cations commonly found in natural systems can be found in Appelo and Postma (2005). They are also included in the PHREEQC-2 database.

PHREEQC uses the Gaines-Thomas convention, which means that the activity of the sorbed species β is defined as the equivalent fraction. For example for CaX_2 :

$$\beta_{\text{Ca}} = \frac{\text{meq}_{\text{CaX}_2}}{\text{CEC}} \quad (4.4)$$

in which $\text{meq}_{\text{CaX}_2}$ is the adsorbed Ca^{2+} concentration expressed in meq/100g and CEC is the *cation exchange capacity*, also expressed in meq/100g. The CEC is a measure of the capability of a material to sorb cations and equals the equivalent sum of all sorbed species. Therefore:

$$\sum \beta = 1 \quad (4.5)$$

Note that equilibrium constants (e.g., Eqn. 4.3) describing ion exchange in the Gaines-Thomas convention use equivalent fraction = 1 for the standard state for each sorbed species but may use either 1 M or

1 m as the standard state for aqueous species. When using equilibrium constants taken from the literature to describe ion exchange reactions, it is important to make sure they are consistent with these standard states.

Equation 4.5 can be conveniently used to calculate the activities of the adsorbed species at a known water composition by combining it with the expressions of the selectivity coefficients (equation 4.3 and similar expressions for other ions). The result is a quadratic expression that can be solved using the abc-formula (Appelo and Postma, 2005).

4.2 PHREEQC Exercise 3: Calculation of the exchange complex composition

In this exercise you will first calculate the composition of the exchanger complex by hand and then with PHREEQC. For the hand calculations you are provided with the concentration of the major cations in seawater (in mmol/kgw):

Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
485	10.6	10.7	55.1

and the selectivity coefficients of K⁺ and Mg²⁺:

$$K_{\text{Na}\backslash\text{K}} = \frac{[\beta_{\text{Na}}][\text{K}^+]}{[\beta_{\text{K}}][\text{Na}^+]} = 0.20 \quad (4.6)$$

$$K_{\text{Na}\backslash\text{Mg}} = \frac{[\beta_{\text{Na}}][\text{Mg}^{2+}]^{\frac{1}{2}}}{[\beta_{\text{Mg}}]^{\frac{1}{2}}[\text{Na}^+]} = 0.501 \quad (4.7)$$

Rewrite equations 4.3, 4.6 and 4.7 to express β_{Ca} , β_{K} and β_{Mg} as functions of β_{Na} and the solute concentrations. Insert into equation 4.5 and solve for β_{Na} . The other values are found by back-substitution. Fill in the values below:

β_{Na}	β_{K}	β_{Ca}	β_{Mg}	$\sum \beta$
.....

You can also use PHREEQC to get the same answer. Enter the cation concentrations as the solution composition and use the keyword **EXCHANGE** to have PHREEQC calculate the exchange complex. The syntax is as follows:

```
EXCHANGE 1
X 0.06
-equilibrate 1
END
```

Under **EXCHANGE**, the concentration of element X is defined. This is the number of exchanger sites in moles. In this case, there are 60 millimoles of exchanger sites. The number in milliequivalents is the same because the exchanger is assumed to have a single negative charge in PHREEQC. Here, the exchanger is in contact with a solution that has 1 kg of water (the default amount in PHREEQC), or 1 l. So, the cation exchange capacity expressed in meq/l is $\text{CEC} = 60 \text{ meq/l}$. Can you calculate how much that is in meq/100g? The answer is $\text{CEC} = \dots \text{ meq/100g}$.

The identifier **-equilibrate** is used to have the exchanger composition calculated by PHREEQC according to equilibrium with a solution. The number after the identifier indicates a solution number, 1 in this case. Alternatively, the solution composition may be entered explicitly by typing the concentrations of the sorbed species. For the purpose of this exercise however, the **-equilibrate** option is required.

The activities of the sorbed species (β) are listed in the PHREEQC output file under the heading ‘Beginning of initial exchange-composition calculations’. Look for the numbers in the column ‘Equivalent fractions’, which are the β values, and insert the appropriate values in the table below.

	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
β
meq/l
K_d

Also insert the sorbed concentrations expressed as meq/l of pore water and calculate the distribution coefficient, K_d . The distribution coefficient is the ratio of the sorbed concentration over the dissolved concentration and is often used in solute transport studies to estimate a retardation factor. The K_d values for seawater are clearly different from the values for a typical fresh water, listed below, which demonstrates the limited applicability of this approach in settings with a strong concentration gradient.

As a final part of this exercise you can also examine the effect of diluting a solution that is in equilibrium with the exchange complex. Because the amount of cations on the exchanger is relatively large compared to the amount of dissolved ions in a dilute solution, the exchanger

tends to work as a buffer. Dillution of the solution will be accompanied by an increase of the monovalent ions relative to the divalent ions, which can be seen by rewriting equation 4.3:

$$K_{\text{Na}\backslash\text{Ca}} \frac{[\text{NaX}]}{[\text{CaX}_2]^{\frac{1}{2}}} = \frac{[\text{Na}^+]}{[\text{Ca}^{2+}]^{\frac{1}{2}}} \quad (4.8)$$

The left-hand side is essentially constant when the sorbed concentrations are large compared to the solute concentration, which means that a 10-fold dillution of Na^+ is accompanied by a 100-fold dillution of Ca^{2+} .

Simulate a 1000-fold dillution of the solution in equilibrium with the exchanger from the previous PHREEQC simulation. You can do this by appending a new simulation in which you equilibrate the exchanger with a new solution that has concentrations 1000 times less than the seawater. Include the following line:

USE exchange 1

to equilibrate the new solution with the exchange complex from the previous simulation. PHREEQC remembers the composition of the exchange complex and the keyword **USE** ensures that the exchanger will be used again in the new simulation.

Inspect your output file and fill in the table below.

Notice that the ratio $\frac{\text{Na}^+}{\sqrt{\text{Ca}^{2+}}}$ has hardly changed after the diluted solution has equilibrated, just as the composition of the exchange complex.

	Na^+	Ca^{2+}	Mg^{2+}
β	0.0169	0.9291	0.054
sorbed (meq/l)	1.014	55.75	3.24
solute (mmol/kgw)	2.43	3.04	0.28
K_d	0.417	9.17	5.79

	Na^+	K^+	Ca^{2+}	Mg^{2+}	$\frac{\text{Na}^+}{\sqrt{\text{Ca}^{2+}}}$
seawater	485	10.6	10.7	55.1	4.69
dill. seawater	0.485	0.0106	0.0107	0.0551	0.148
dill. + equil.
sorbed (meq/l)	
sorbed (meq/l)	

Table 4.1: Flow and transport parameters used for PHT3D Exercise 4.

Flow simulation	steady state
Total simulation time (<i>days</i>)	3000
Time step size	40
Model length (<i>m</i>)	100
Model thickness (<i>m</i>)	10
Grid spacing Δx (m)	4
Grid spacing Δz (m)	0.5
Porosity	0.35
Horizontal hydraulic conductivity (<i>m</i>)	1 m/d
Vertical hydraulic conductivity (<i>m</i>)	1 m/d
Piezometric head upstream boundary (<i>m</i>)	12 m
Piezometric head downstream boundary (<i>m</i>)	10 m
Longitudinal dispersivity (<i>m</i>)	2.5
Transverse vertical dispersivity (<i>m</i>)	0.025

4.3 PHT3D Exercise 4: Transport and nitrification of ion exchangeable ammonium

This modelling example is based on a field site contamination problem near Mansfield UK (see, e.g., Broholm et al., 1998; Davison, 1998; Jones et al., 1998; Davison and Lerner, 2000; Jones and Lerner, 2001), 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 Haerens (2004). 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 already set up, except for the cation exchange process.

Table 4.2: Concentrations of aqueous components and initial mineral concentration in PHT3D Exercise 4.

	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	

4.3.1 Running MODFLOW and PHT3D

To run MODFLOW and PHT3D, proceed as follows:

- Copy the ORTi file for this exercise and the database file from the google drive folder
- Load the provided ORTi model and inspect the model input.
- Now run MODFLOW to regenerate the flow-file (mt3d.flo), which will subsequently be used by the reactive transport model.
- Inspect the simulated hydraulic heads - make sure the results are plausible

- To run PHT3D go to [Parameters](#) → [Chemistry](#) and use the [Write 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 simulation results are plausible.
- Now plot also the breakthrough curves for the cations Amm, Ca, and Na at $x = 50$ m and $z = 7$ m.
- To do this use ORTi's multiplot functionality, where it is possible to visualise several species simultaneously for both simulated and observed concentrations. You will notice the obvious disagreement between simulated and observed concentrations.

To improve the agreement between observed and simulated data we now consider cation exchange reactions. To include this process in the reaction 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 activate [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, 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.

Chapter 5

Surface complexation reactions

5.1 Background

Oxides, hydroxides and organic matter carry functional groups at their surface, which enable them to sorb cations, anions, and neutral species from solution. Typically, these functional groups behave as Bronsted acids and/or bases, which is to say they can accept hydrogen ions, release hydrogen ions, or, in some cases, both. The sorption behaviour depends on the type of mineral, crystal morphology, even which crystal face(s) dominate, as well as the composition and pH of the solution. In response to uptake/release of hydrogen or other ions from/to solution, a net charge on the surface develops.

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

$$\log K_a = \log K_{\text{int}} + \frac{zF\psi_0}{RT \ln 10} \quad (5.1)$$

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 (Parkhurst and Appelo, 1999).

5.2 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 m²/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: $K_d = \dots\dots\dots$

Test the effect on the K_d of:

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

5.3 PHT3D Exercise 5, Zinc transport at the Cape Cod site

In this exercise we will construct a model that provides a good example for the consideration of surface complexation reactions in PHT3D. The example is based on a modelling study for the Cape Code site. The full details of this study were reported in Kent et al. (2000). The Cape Cod research site is near a wastewater-treatment facility at the Massachusetts Military Reservation (MMR). A treated-sewage plume originated from the facility's infiltration beds, which were used from about 1936 to 1995. At the time the modelling study was undertaken the plume at the site extended more than 6 kilometers from the disposal site in the sand and gravel aquifer. The plume contains a complex mixture of phosphate, nitrate, metal ions (such as zinc), detergents, organic chemicals, and microbes. Over many years the plume and adjacent parts of the aquifer served as a field laboratory for a multidisciplinary team of scientists who investigated many fundamental aspects of contaminant transport behaviour.

5.3.1 Background: Groundwater Flow

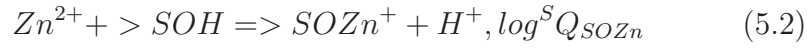
At the Cape Cod site the regional groundwater flow is generally towards the south, but locally the flow direction is directed from the sewage treatment facility towards the eastern shore of Ashumet Pond. The groundwater flow is nearly horizontal. Approximately 25 cm/yr of areal recharge results in a small vertical component to flow as well as in the accumulation of a lens of pristine groundwater on top of the sewage plume, the thickness of which increases with distance away from the sewage treatment plant (Leblanc, 1984, 1991). The magnitude of the hydraulic gradient is approximately 1.7 m/km. Seasonal fluctuations in the flow system result in small variations (approximately 0.2 m/km) in the magnitude of the gradient as well as in small annual fluctuation in flow direction.

5.3.2 Background: Hydrogeochemistry

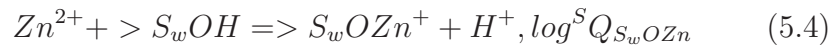
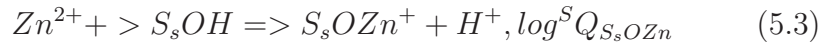
Contrasting chemical conditions between sewage-contaminated and ambient groundwater gave rise to longitudinal and vertical gradients in groundwater chemistry. The ambient groundwater surrounding the sewage plume had high concentrations of dissolved oxygen, pH values in the range 5.3-5.8, and low concentrations of dissolved salts (Leblanc, 1991; Hess et al., 1996; Kent and Maeder, 1999). Sewage-contaminated groundwater under the disposal beds had high concentrations of nitrate.

Concentrations of dissolved oxygen successively decreased with depth (Smith et al., 1991a,b). Biodegradation of organic matter in conjunction with solute transport away from the disposal beds resulted in the depletion of dissolved oxygen throughout the plume and the depletion of nitrate, followed by the accumulation of dissolved Fe(II), in the core of the plume (Smith et al., 1991a; Kent et al., 1994).

These biodegradation reactions influenced the pH within the aquifer zone affected by the sewage plume (??). The principal chemical process in terms of controlling Zn transport is assumed to be Zn adsorption onto the sediments. A single reaction with the stoichiometry could already adequately describe the pH effect observed in laboratory batch studies of Zn adsorption onto the sediments (Davis et al., 1998):



Adding a second surface site with the same reaction stoichiometry results in an SCM that can fit both the pH and Zn-concentration effect (Davis et al., 1998). This so-called two-site approach was one of the various numerical implementations tested by Kent et al. (2000). This two-site model will be used in the present exercise. In the two-site SCM a small percentage of the total adsorption sites are considered to have a much greater affinity for adsorption ("strong sites," $> \text{SsOH}$) than the rest of the sites ("weak sites," $> \text{SwOH}$):



Before proceeding, it is worthwhile to consider the standard state for sorbed species in surface complexation models. The same standard state used for aqueous species - either 1 mole of surface complex \L of solution (M) or \kilogram water (m) - is often used for surface complexes as well. For example, the comprehensive compilation of equilibrium constants for sorption on hydrous ferric oxide by Dzombak and Morel (1990) adopts a standard state of 1 M for sorbed species. One should be aware, however, there is a pitfall associated with this choice of standard state (e.g., Appelo and Postma, 1999). The pitfall can be illustrated by considering a batch reactor with a suspension in sorptive equilibrium. In this thought experiment, we allow all of the solids to settle to the bottom of the reactor once sorptive equilibrium has been achieved, then we remove half of the solution without removing any solid. Sorbed concentrations expressed in moles/kg water have now increased by a factor of two because the volume of solution (hence, mass of water)

has decreased by a factor of two with no change in the amount of the solid. For surface complexation reactions such as those described the Eqn. 5.3 and Eqn. 5.4, the concentration of sorbed Zn doubles and the concentration of free surface functional groups double, so the factor of two cancels out in the mass action expression. For this type of surface complex - called "monodentate" (one surface site per sorbed species) - the choice of standard state for sorbed species does not affect the value of the equilibrium constant. However, for "bidentate" surface complexes, where there are two surface functional groups bound to a single sorbing species, the situation is more complicated. Consider formation of a bidentate surface complexation analogous to Eqn. 5.3:



The mass action expression can be written with the concentration of the Zn surface complex raised to the first power in the numerator and concentration of free surface sites squared in the denominator. In this mass action expression, the factor of two does not cancel out. This observation can be generalized by stating that equilibrium constants describing sorption where multidentate surface complexes are involved are a function of the solid to liquid ratio if a standard state of 1 M or 1 m is adopted for sorbed species. There has been much discussion of this in the literature (e.g., Wang and Giammar, 2013). To avoid this pitfall, PHREEQC adopts a standard state for sorbed species whereby the fraction of sites occupied by a given sorbed species equals 1. In reaction 5.5, the relationship between sorbed Zn in units of moles \kg water and sorbed Zn in units of mole fraction occupied sites is

$$X\text{Zn} = 2[(> \text{S}_s\text{O})_2\text{Zn}]/[\text{S}_s\text{OHT}], \quad (5.6)$$

where square brackets refer to concentrations in moles/kg water and SsOHT is the total concentration of strong sorption sites. The factor of two results from the fact that the surface complex covers two sites. Therefore, when using equilibrium constants for multidentate sorbed species taken from the literature in a transport simulation, it is important to insure that either the equilibrium constant uses mole fraction of sites occupied by any given sorbed species = 1 or is properly converted to that standard state. Formulas for making such conversions are presented in various papers (e.g., Wang and Giammar, 2013).

With the sorption and thus the mobility of Zn being strongly dependent on pH, it is important to accurately capture the pH-controlling processes. For the vertical transect model that will be constructed in this exercise the evolution of the pH will mostly be affected by (i)

the transport and mixing of two different water types, i.e., of the (upstream) water composition and the slightly more acidic (pH = 5.6) groundwater recharge water and (ii) the pH increase that is induced by the degradation of organic matter in conjunction with sulfate and iron reduction. The former causes a pH gradient that is the result of physical transport processes. The latter causes inside the plume-affected aquifer zone a pH increase towards 6.5, and thus above the pH of 6.0 that characterises the uncontaminated background water. For this exercise the organic matter degradation is represented in a simplistic way by a single kinetically controlled degradation reaction of DOC in conjunction with the reduction of two electron acceptors sulfate and goethite. It is assumed that nitrate is already depleted at the model's upstream boundary and thus not considered. The rate r_{DOC} of the DOC mineralisation is computed from:

$$r_{DOC} = \frac{C_{DOC}}{K_{DOC} + C_{DOC}} \sum_{i=1, n_{REA}} k_{EA_i} \frac{C_{EA_i}}{K_{EA_i} + C_{EA_i}} \quad (5.7)$$

where C_{DOC} is the DOC concentration, C_{EA_i} is the concentration of the i^{th} electron acceptor (in the present case either sulfate or goethite) while K_{DOC} and K_{EA_i} are half saturation constants for DOC and the i^{th} electron acceptor, respectively.

In reality the composition of the sewage plume and the reactions are obviously far more complex, as discussed in detail by Kent et al. (2000). Nevertheless, the inclusion of this reaction allows to replicate some of the key features observed at the site, and, most importantly, allows to mimic the observed pH patterns relatively well. Therefore the model constructed in this exercise also reproduces the major Zn transport patterns relatively well, i.e., the rates of Zn movement and the vertical differences in the mobility, as induced by the spatial variability of the pH.

5.3.3 Setting up the flow model

To set up the flow model proceed as follows:

- In ORTI, create a new model and save it in a new and separate directory (folder).
- Select [Parameters](#) → [1.Model](#) → [Model](#) to specify the model dimension ('Xsection') and type ('free')
- Select [Parameters](#) → [1.Model](#) → [Domain](#) to specify the domain as described in Table 5.1. For the first simulation select a spacing of 20 m in x direction and 1 m in y direction

- Select [Parameters](#) → [Time](#) → and set the [Total Simulation Time](#) to 21000 days. Then define the step size to 60 days
- Set the boundary conditions for heads by selecting [Spatial Attributes](#) → [MODFLOW](#) → [bas.3 Boundary Conditions](#) corresponding to IBOUND (Modflow). Use the [Zone Tool](#) to create a zone at the outflow end that extends vertically between $z = 0$ m and $z = 13.9$ m.
- To fix the hydraulic heads at the boundaries, use [Spatial Attributes](#) → [MODFLOW](#) → [bas.5 Initial Heads](#) and provide a value of 16 in the dialog box. This value will be used everywhere as a starting (initial) head and will be kept at this value at all locations where a fixed head boundary condition was defined in the previous step. In order to fix the heads at the outflow boundary, draw a line at the same location as the outflow BC and attribute a head value of 14 m.
- The inflow boundary is implemented by a single well that vertically extends between 0 and 15 m. The total injection rate of this well should be set to $2.16 \text{ m}^3/d$.
- Select [Parameters](#) → [2.Flow](#) → [Parameters](#) and use this dialog to set several parameters. In [lpf.2](#) select [Convertible](#) for the [type of](#)

Table 5.1: Flow and solute transport parameters used for the setup of PHT3D Exercise 5

Parameter	Value
Flow simulation type	steady state
Simulation time (days)	21000
Time step (days)	60
Model extent column direction (m)	400
Model top elevation (m)	16
Model bottom elevation (m)	0
Horizontal hydraulic conductivity (m/day)	110
Porosity, θ	0.39
Piezometric head downstream boundary (m)	14
Longitudinal dispersivity, α_L (m)	1.0
Horizontal transverse dispersivity, α_{TH}	0.1
Vertical transverse dispersivity, α_{TV}	0.01
Effective diffusion coefficient, D^*	0

layer. Then use [lpf.8](#) to specify the hydraulic conductivity.

- To fix recharge, use [Spatial Attributes](#) → [MODFLOW](#) → [rch.2 Recharge](#). Create a zone along the top cells and define a value of 0.0014 in the dialog box.
- To define the porosity select [Spatial Attributes](#) → [MT3DMS](#) → [btn.11](#) and set [Value](#) to 0.39.

Regularly save the changes to avoid loss of your data input.

5.3.4 Running MODFLOW

You have now completed the set up the flow model and are ready to run MODFLOW. This step will provide PHT3D with the flow field that will be used to simulate reactive transport.

- Select [Parameters](#) → [2.Flow](#) → [Write](#)
- Select [Parameters](#) → [2.Flow](#) → [Run](#)
- When the calculations have finished, a new window will appear. I will show the last line(s) of the MODFLOW output file. Make sure MODFLOW terminated without errors.

5.3.5 Visualising hydraulic heads

- Visualise results by selecting [Results](#) → [2.Flow](#) → [Head](#). The time step can be changed in [Results](#) → [1.Model](#) → [Time](#).
- Assess if the head distribution is plausible.

5.3.6 Chemistry

In this section we will define (i) the initial hydrochemical composition (ii) the solutions that represent the sewage plume composition at the upstream model boundary and (iii) the groundwater recharge composition. Proceed with the following steps:

- Import the database from the folder that contains the Supporting Information for this exercise
- The species needed to be activated are *Cl*, *C(4)*, *Fe(2)* and *Fe(3)*, *Na*, *O(0)*, *S(-2)* and *S(6)*, *Orgc*, *Zn* and, as always, *pH* and *pe*. As described in the previous PHT3D Examples, the activation of these species/componenets and the definition of the solution

compositions are done in the [Solution Tab](#). All required concentrations are listed in Table 5.2.

- It is assumed that goethite is present at a (background) concentration 0.1 mol/L_b . FeS(ppt) must also be ticked. It is initially not present and thus the concentration is left at the default value of 0.
- The allocation of the solutions to define initial and boundary conditions can be done via [ph.4 Source / Sink](#) zones (line). To allocate the correct solutions at the inflow boundary allocate from 14 m to 16 m *Solution 2*, from 3 m to 14 m allocate *Solution 1* and between 0 m and 3 m allocate the background solution, i.e., *Solution 0*.
- The groundwater recharge composition is entered via [ph.5](#) as a line along the top grid cells. The recharge water composition is defined by *Solution 3*. However, make sure that the recharge does not extend to the cell at the inflow end of the grid.
- Under the [Rates Tab](#) specify the degradation rate parameters for Orgc (0,1e-11, 1e-12, 1e-12,1e-17,1e-17 respectively) and also enter the stoichiometry of the mineralisation reaction. The formula is Orgc -1.0 CH₂O 1.0.
- Activate both available types of surface sites, i.e., S_s and S_w . Define $1.59\text{e-}5 \text{ mol/L}_b$ and $.0018 \text{ mol/L}_b$ as their respective background concentrations.

5.3.7 Running PHT3D

With the model setup completed run PHT3D and visualise the results via contour plots.

Table 5.2: Chemical composition for PHT3D Exercise 5

Parameter	Background	Solution 1	Solution 2	Solution 3
C(4)	1e-4	1e-4	1e-4	1e-4
Cl	0	0	0	1e-4
Fe(2)	0	0	0	0
Fe(3)	0	0	0	0
Na	2.3e-4	2.3e-4	2.3e-4	3.13e-4
O(0)	5e-4	0	5e-4	5e-4
Orgc	0	1e-4	0	0
S(6)	1e-4	1e-4	1e-4	1e-4
S(-2)	0	0	0	0
Zn	0	8e-6	8e-6	0
pH	6	6	6	5.6
pe	14.6	4	14.6	14.2

5.4 PHT3D Exercise 6 Transport of uranium in a fractured rock aquifer

In this exercise we will investigate the transport of solutes in a fractured aquifer system. The exercise will illustrate how the dual-domain mass transfer model (DDMT) can be used to mimic the characteristic physical transport behaviour of fractured rock and how the model mass transfer with the matrix may influence the transport of uranium. The illustrative example is defined for a case in which the potential impact of the release of mining wastes on a surface water body is investigated. The main focus is on understanding the coupled physical and chemical transport behavior of uranium.

5.4.1 Groundwater flow

The model for the site consists of a cross section that follows a principle flow path between the groundwater divide and a discharge point to a creek that is located 2 km downstream of the groundwater divide. Groundwater recharge from rainfall is the only driver of groundwater flow in this situation and all recharged water eventually discharges to the creek. The aquifer is unconfined and the groundwater table is controlled at the downstream boundary by the water level of the creek. This is implemented in the model through a specified head boundary. The upstream end of the model, i.e., the groundwater divide is implemented through a no flow boundary. Similarly the base of the aquifer and the vertical boundary at the creek's position are implemented as no flow boundaries. The completed groundwater flow model will be provided to you and form the starting point of this exercise.

Save the files supplied for this exercise (ORTI file and database file) in a newly created folder. Then open the file **dd_u.orti**. Before running the model, inspect the model and check

- the position of the boundary condition under **Spatial attributes** → **Modflow** → **Bas.3**
- the initial and specified heads **Spatial attributes** → **Modflow** → **Bas.5**
- the implementation of groundwater recharge under **Spatial attributes** → **Modflow** → **Rch.1**
- the length of the simulation under **Parameters** → **Model** → **Time**

In the next step write the MODFLOW input files and run MODFLOW. Verify that the **Total Time** shown in the pop-up window is the same as your user-specified simulation time. If it differs the model run was not successfully terminated and the model needs to be debugged. Inspect the simulation results.

5.4.2 Conservative solute transport in a single domain

Before simulating the reactive transport of uranium we will first investigate the transport behavior of a conservative tracer between a pit that is filled with tailings material and the point of groundwater discharge to the surface water. This will allow a first estimate of the travel-time and of the degree to which mixing and dispersion causes a concentration attenuation for any solutes that are transported between the pit and the discharge zone. In a first step the simulation will be performed under the assumption that the aquifer can be described as a media behaving equivalent to a porous media. For these first model simulation the tracer is added across the whole volume of water representing the tailings fluids.

To run this first conservative transport model follow these steps:

- check the duration of the simulation (parameters/model/time). It should be 73000 days (approximately 200 years).
- set the position of the pit for the initial concentration of the tracer. We will suppose that the initial concentration is homogeneous over the whole pit. To do this go to **Spatial attributes** → **Mt3dms** → **Btn.13** concentrations and create a zone, that extends from 501 to 799 m in x direction and 60 to 89 m in z direction. Set a value of 10 for the tracer. This can be any unit.
- Set the porosity to a low value (0.02) corresponding to the fractures, in **Spatial attributes** → **Mt3dms** → **Btn.11**
- Set the longitudinal dispersivity to 1m under **Parameters** → **Transport** → **Parameters** → **Dsp.2** and leave the ratio of transverse to longitudinal at it default value.
- Then write the Mt3dms input files and run the model

After the model run, look at the temporal evolution of the concentrations in the domain to assess the time it takes to deplete the tracer from the pit. To view the potential tracer output to the creek, go to **Results** → **Observations** → **Breakthrough** → **Creek_obs** and select **Value**. This will plot the breakthrough curve of the tracer at the

point of discharge to the creek. Export the results to a text file such that the data can later be used for a comparison of different cases.

5.4.3 Conservative solute transport in a dual-domain system

Up to now groundwater flow was considered to occur more or less homogeneously in a porous medium. However, in fractured rock the vast majority of the water flux occurs in the fractures while the water prevailing outside the fractures can be considered as immobile. The exchange of solutes between the mobile fraction of the aquifer, i.e., the fractures and the immobile domain (i.e., matrix) occurs slowly. In many cases mass exchange is limited to transport by molecular diffusion. This can be modelled by invoking the **RCT** package in MT3DMS. In the **RCT** package two major adjustments have to be made, i.e., the total (single) porosity has to be replaced by a combination of a mobile and an immobile porosity. Additionally the exchange coefficient between the mobile domain and the immobile domain has to be defined.

- First add the **RCT** package to the suite of modules that can be used in your simulation. To do this go to **Menu** → **Addins**, select **Mt3dms modules** and check the **RCT** package. This will enable the **Spc** and the **Rct** buttons to appear under **Parameters** → **Transport**.
- Go to **Parameters** → **Transport** → **Parameters** → **RCT** → **Rct.1 Major Flags** and set the **ISOTHM** value to **dual domain no sorption**. Furthermore, keep **no reaction** and set the **initial conc** to **Given**, before clicking **Apply**.
- Then, in the same panel, go to **Rct.2b** and set the **immobile porosity** to 0.23, the value that represents the porosity of the immobile domain. Click **Apply**
- Also in the same panel go to **Rct.2c** and set the **initial concentrations** to 0 to define that the initial concentration of the tracer in the matrix is null.
- We have to specify which species will be submitted to dual domain exchange. To do this click on the **Parameters** → **Transport** → **Spc** button, and in the dialog select **Mt3dms** and add **Tracer** as the species name.
- The exchange coefficient value is provided by using the **Parameters** → **Transport** → **Rct** button, which opens a grid dialog that only shows **Tracer** in this incidence. The mass transfer coefficient

which controls the rate at which mass is exchanged between the mobile and immobile domain can be entered in the **SP2** column. Try a low value such as $5.10 \times 10^{-06} d^{-1}$. The exchange coefficient employed here is set to a small value because the matrix porosity, i.e., the water-filled pore space not occupied by the fractures is made of very small pores and fissures. However, over long transport timescales such as in the present case the effect of matrix diffusion can still be significant.

- Finally write the MT3DMS input files and run MT3DMS.

To compare your results to the previous single domain simulation display the breakthrough curves again (i.e., **Tracer** for the same observation point **creek_obs** as above), export the concentration and compare the two breakthrough curves in excel.

If you have time

- Think about what are the major differences between the simulated breakthrough curves ?
- Rerun the model with with different mass transfer coefficients, For example, run a variant with a 10-times higher mass transfer coefficient and another variant with a 10-times lower mass transfer coefficient.
- Interpret the differences between the different types of breakthrough behavior that is generated by the different model variants.

5.4.4 Multi-component transport in a dual-domain system

Following from the (conservative) tracer transport simulations the next step in this exercise is to expand the model to jointly simulate the transport of all major groundwater constituents that may play a role for the evolution of the hydrochemical patterns in the aquifer. Initially we will not consider any water rock interactions and the first multi component simulation will only consider aqueous complexation reactions. For simplicity we consider only two types of water compositions.

First we consider the ambient groundwater composition, to which we refer to as **background solution**. Secondly, we consider the composition of the tailings fluids, which we refer to as **Solution 1**. For simplicity we assume that the tailings fluids have the same composition throughout the entire pit. Both compositions are listed in Table 5.3. To establish the first multi-component simulation

- import the database file that is provided for this example by going to **Parameters** → **Chemistry** → **ImpDb - Import Database**. This database includes most of the important uranium species that could be relevant for this type of problem.
- go to the **Parameters** → **Chemistry** → **Chemistry** button to enter the two aqueous solutions compositions listed in Table 5.3. The corresponding aqueous components need to be activated. Note, that all components that have an initial concentration of zero will also need to be activated (i.e., ticked) as they can be produced by geochemical reactions during the simulation.

The next step will be to assign the two defined aqueous solutions, i.e., **background solution** and **Solution 1** as initial and boundary conditions. By default the **background solution** is used to assign the initial concentrations throughout the entire model domain. However, **Solution 1** has to be assigned to the specific zone in the model that represents the location of the pit, which contains the tailings fluids. We will use the same zone for the pit as the one we used in the conservative transport simulations.

In order to do this,

- go to **Spatial attributes** → **Mt3dms** → **btn.13** and select in the **Modify zone** panel, the zone that you created for the pit. Click on the **Value** button, and copy the coordinates (using **Ctrl+C**).
- Then go to **Spatial attributes** → **Pht3d** → **Ph.3** and select **Initial chemistry** to create a new rectangular zone that represents the location of the pit. Once the dialog for the zone characteristics opens, go to the input zone for the zone coordinates and paste the previously saved coordinates (using **Ctrl +V**) to this location. Note, that pasting only works if the target cells are selected and not the cell content. Before leaving this Tab verify that your coordinates are copied correctly. Should cut and paste not work properly you can simply manually modify the coordinates to those used in the tracer simulation. For the **zone value**, assign the value **1.0.0.0**, which means you assign the water composition defined defined **Solution 1** to this zone, together with the Phase/Mineral assemblage **0**, Exchanger **0** and Surface **0**. All of the latter contain any activated entities and therefore no water-rock or water-sediment interactions are activated. The defined concentrations will be used as initial concentrations at the start of the simulation.

Generally the physical transport parameters to be used in the multi-component PHT3D simulation (such as the longitudinal dispersivity) will be automatically adopted from the previously defined MT3DMS input. However, some modifications have to be made with respect to the settings that control the dual-domain transport behavior. First, we need to specifically list all aqueous components that will be affected by the dual-domain mass transfer process and secondly we need to define the mass transfer coefficient for each of the aqueous components. With rare exemptions all the aqueous components that are included in the reaction network will be affected by the dual-domain mass transfer. In order to define the dual-domain mass transfer for the multi-component simulation

- First click on the **Parameters** → **Transport** → **Spc** button and specify **Pht3d** instead of the previously used **Mt3dms**. Then in the dialog box you will need to enter the names of all components that are included in the reaction network. Note, that the spelling has to be identical with the spelling used in the database. You can, for example, prepare the list in excel or notepad and then copy and paste it into the dialog box.
- Then click on the **Rct** button that is located next to the **Spc** button. You shall see there all the names of the components that you just entered. Then in the **SP2** column specify the exchange coefficient to a value of $5.10 \times 10^{-06} \text{ d}^{-1}$ for all listed components, including **pH** and **pe**.

Once this input is completed the PHT3D input files can be written and PHT3D can be executed. You will notice that the PHT3D simulation will proceed much more slowly than the MT3DMS simulation. The reason is that PHT3D has to compute the solute transport for all included aqueous components and additionally the geochemical reactions. So it is generally wise to carefully verify the model input before running the model. If required, it is possible to stop the simulation with **Ctrl+C**. If needed, the intermediate results that were computed up to the last simulation time can then be visualised. This can be useful when a first quick check is required.

Once the model simulation is terminated inspect the transport behaviour of uranium. To do this visualise the 2D plume contours and plot the breakthrough curve.

- What is the maximum uranium concentration discharging to the creek ?

- Compare the arrival time of the uranium peak with the peak of the previous MT3DMS **Tracer** simulation.

Table 5.3: Aqueous concentrations of the ambient groundwater (Background solution) and of the tailings fluid (Solution 1).

Aqueous component	$C_{Background}$ ($mol\ l_w^{-1}$)	$C_{Solution1}$ ($mol\ l_w^{-1}$)
pH	6.67	4.70
pe	4	4
Na	6.16×10^{-5}	5.24×10^{-3}
Cl	6.13×10^{-3}	1.48×10^{-2}
K	5.12×10^{-5}	4.61×10^{-3}
Ca	1.15×10^{-3}	5.23×10^{-3}
Mg	5.50×10^{-3}	4.44×10^{-1}
Al	1.00×10^{-4}	5.23×10^{-3}
Amm	0	2.85×10^{-2}
C(4)	1.88×10^{-3}	1.40×10^{-5}
Mn(2)	0	2.86×10^{-2}
Mn(3)	0	0
S(6)	2.94×10^{-3}	4.92×10^{-1}
S(-2)	0	0
Si	4.00×10^{-3}	3.03×10^{-4}
Uranyl	8.00×10^{-7}	3.14×10^{-5}

5.4.5 Development of surface complexation model

Experimental data

Cores were collected from a fractured rock aquifer adjacent to a uranium mine. The cores were collected near a pit from the mine that had been backfilled with wastewater water and waste-rock from processing to extract the uranium. Processing the ore involved extraction with sulfuric acid and ammonia.

The specific surface area of the material determined by N_2 adsorption was $15\ m^2/g$ and the sorbed U(VI) concentration on the material determined by carbonate extraction (Kohler et al., 2004) was $80\ nmol/g$.

The compositions of the groundwater from the fracture zone and of water from the pit were determined and used to prepare artificial solutions for conducted U(VI) sorption-desorption experiments. The

pit-water and groundwater were considered to represent end members of the solution compositions that would result from pit-water entering the fracture zone. Experiments were conducted in artificial pit-water, artificial groundwater, and two other groundwater compositions prepared, based on mixing calculations of the two end members. The end-member artificial groundwater was designated AGW1, the artificial pit-water APW, the two mixtures AGW3 and AGW4. Compositions were presented in Table 5.4

Table 5.4: Synthetic solutions used in U(VI) sorption-desorption experiments. All concentrations are in moles per liter except pH and P_{CO_2} .

Aqueous component	C_{AGW1} ($mol\ l_w^{-1}$)	C_{APW} ($mol\ l_w^{-1}$)	C_{AGW3} ($mol\ l_w^{-1}$)	C_{AGW4} ($mol\ l_w^{-1}$)
pH	6.64	4.70	6.50	6.76
Alkalinity	4.05×10^{-3}	0	3.65×10^{-3}	3.93×10^{-3}
Na	1.26×10^{-4}	5.00×10^{-3}	6.13×10^{-4}	2.72×10^{-4}
K	5.10×10^{-5}	4.40×10^{-3}	4.86×10^{-4}	1.82×10^{-4}
Mg	1.97×10^{-3}	3.00×10^{-1}	3.18×10^{-2}	1.09×10^{-2}
Ca	1.15×10^{-4}	5.00×10^{-3}	6.04×10^{-4}	2.62×10^{-4}
Amm	0	3.50×10^{-2}	3.50×10^{-3}	1.05×10^{-3}
Mn(2)	0	2.70×10^{-2}	2.70×10^{-3}	2.00×10^{-5}
Zn	0	1.50×10^{-4}	1.50×10^{-5}	5.00×10^{-6}
Uranyl	8.00×10^{-7}	3.08×10^{-5}	3.80×10^{-6}	1.80×10^{-6}
Cl	0	1.00×10^{-2}	1.00×10^{-3}	3.00×10^{-4}
N(5)	0	6.00×10^{-5}	6.00×10^{-6}	2.00×10^{-6}
S(6)	1.50×10^{-4}	3.49×10^{-1}	3.50×10^{-2}	9.80×10^{-3}
P_{CO_2}	3.50×10^{-5}	4.00×10^{-4}	3.50×10^{-5}	3.50×10^{-5}

All experiments were conducted at a solid/liquid ratio of 10 g/L at 25 degrees C. Experiments with AGW1, AGW3, and AGW4 were conducted so that equilibrium with a P_{CO_2} of 0.035 atmospheres was maintained. Experiments with APW were conducted in equilibrium with the atmosphere (0.00040 atmosphere). After steady concentrations of U(VI) were observed, the suspensions were considered to be at equilibrium.

The total U(VI) concentration in each experiment was calculated from the U(VI) added in the aqueous phase and the sorbed U(VI) added with the solid phase. Total U(VI) concentrations and the sorbed U(VI) concentrations at equilibrium are presented in Table 5.5.

Table 5.5: Total U(VI) concentrations and sorbed U(VI) concentrations at equilibrium in each of the solution used in the experiments.

Solution	Total U(VI) ($mol\ l_w^{-1}$)	Dissolved U(VI) ($mol\ l_w^{-1}$)	Sorbed U(VI) ($mol\ l_w^{-1}$)
AGW1	8.00×10^{-7}	1.90×10^{-7}	6.10×10^{-7}
APW	3.08×10^{-5}	2.16×10^{-5}	1.06×10^{-5}
AGW3	3.80×10^{-6}	1.40×10^{-6}	2.40×10^{-6}
AGW4	1.80×10^{-6}	1.25×10^{-6}	5.50×10^{-7}

Table 5.6: Possible surface complexation reactions to fit the experimental data.

Surface reaction
$SOH + UO_2^{2+} + H_2O + CO_2 = SOHUO_2HCO_3^+ + H^+$
$SOH + UO_2^{2+} + H_2O + CO_2 = SOUO_2H_2CO_3 + 2H^+$

Site-specific surface complexation model

To describe the experimental data perform the following steps

- Choose one of the two surface complexation reactions in Table 5.6.
- Fix the total site concentration at 5.76×10^{-4} .
- Use a non-electrostatic model.
- Fit the sorbed U(VI) concentration in Table 5.5 by adjusting the logK value.
- Find the logK value that you think provides the closest fit to the experimental data.
- You may use the provided Phreeqc input and the provided Excel file

Note, that neither of the reactions in Table 5.6 will provide a perfect fit to the experimental data

5.4.6 Impact of surface complexation reactions in the field-scale model

In the next step we will investigate how sorption of uranium affects the overall uranium migration patterns. To do this we will activate the

surface complexation model that was developed for this site.

- Go to **Parameters** → **Chemistry** → **Chemistry** and select **Surface**. Now, activate the surface with the name **Surf_a** and enter 2.0×10^{-4} as the surface site concentration under **Site_back**. As we define this concentration as background concentration it will be applied throughout the model domain. The initial occupancy of the surface sites will be automatically determined at the start of the simulation, i.e., there will be an equilibration step that makes sure that the aqueous composition(s) and the surface(s) are in equilibrium. The presence of the surface sites will cause the aqueous uranium that migrates away from the pit to undergo surface complexation reactions, with the variable extent of the sorption being a function of the spatially and temporally variable geochemical conditions.
- The present model is using the **no.edl** option, which means that the surface complexation reactions do not consider any electric double layer effects. If required, this can be changed under **Parameters** → **Chemistry** → **Parameters** → **PH** → **ph.6** where a different option such **-ddl** could be entered.

Now rerun PHT3D and investigate how much the sorption reactions have impacted the uranium transport behavior. Note, that the correct up-scaling of the laboratory results to the field-scale model is a non-trivial task and still an area of active research. Up-scaling needs in particular to take into account the changes in liquid to solid (i.e., number of surface site) ratio between the samples investigated in the laboratory and the field conditions. The number of sites used here (2.0×10^{-4}) is at the lower (conservative) end of the range for this value. You can study the strong impact of this parameter on the breakthrough behaviour of uranium by rerunning the model with a 10-fold increased surface site concentration of 2.0×10^{-3} .

5.4.7 Impact of mineral buffering

So far we have excluded mineral reactions and therefore not considered the potential impact of pH buffering reactions on raising the pH of the aqueous solution that emerges from the tailings pit zone. In the next step we add chlorite to the background mineral assemblage.

To implement chlorite

- Go to **Parameters** → **Chemistry** → **Chemistry** and select **Phase**. Now, activate chlorite and enter a background concen-

tration of 0.1 mol/L under **Backgr. Moles**, i.e., in the second column.

- Then go to **Spatial attributes** → **Pht3d** → **Ph.3** and select **Initial chemistry** to define that chlorite is not present in the pit zone. Change the previously entered value **1.0.0.0** to **1.1.0.0**. This means that you now assign the Phase/Mineral assemblage **1** to this zone. As the chlorite concentration for Mineral assemblage 1 is zero the initial chlorite concentration that will be used for the pit zone will also be zero.

Now rerun the model and investigate the impact on the uranium transport behavior.

5.5 PHREEQC Exercise 5: Site-specific surface complexation model for As

In this exercise, we will use PHREEQC to develop a model that can quantitatively describe the site-specific sorption characteristics of natural sediment material collected from a Pleistocene aquifer near Hanoi, Vietnam. This can be done by formulating a set of surface reactions and by adjusting the log_{ks} of those reactions until they match the experimental data that were collected from anaerobic laboratory batch experiments. Even though this example is focused on arsenic, the procedure itself is more generally applicable to a wide range of metals and metalloids. Both the sorption experiments and the SCM development for the Pleistocene sands are described in more detail by Rathi et al. (2017). The measured data suggest that *As(III)* sorption on the sediments increased non-linearly and phosphate ions competed strongly with *As(III)* for adsorption. The SCM employed to describe these data is a generalized composite model, as proposed by Davis et al. (1998). In this approach a generic surface site ([Site_sOH](#)) is thought to be responsible for adsorption of both *As(III)* and $PO_4 - P$. Note, that these modelled sites are not associated with a particular mineral phase of the Pleistocene sediments but represent the overall sorption behaviour of the entire mineral assemblage.

Table 5.7: Adjustable parameters, including surface complexation reaction constants for *As* and sorption site density.

Reaction / Parameter	Best value
$Site_sOH + As_threeO_3^{3-} + 3H^+ = Site_sH_2As_threeO_3 + H_2O$	43.665
$Site_sOH + As_threeO_3^{3-} + 2H^+ = Site_sHAs_threeO_3^- + H_2O$?
$Site_sOH + PO_4^{3-} + 3H^+ = Site_sH_2PO_4 + H_2O$	31.281
$Site_sOH + PO_4^{3-} + 2H^+ = Site_sHPO_4^- + H_2O$	29.065
$Site_sOH + PO_4^{3-} + H^+ = Site_sPO_4^{2-} + H_2O$	15.393
<i>Site density</i>	?

The PHREEQC input file [as_scm_wrr2017.phrq](#) that controls the model simulations and the two files containing experimental data ([as_iso.tsv](#) for *As(III)* and [as_po4.tsv](#) for PO_4) have been prepared for you.

SURFACE 1

[Site_sOH](#) #enter value#

-no_edl
END

As can be seen, the model uses the **no_edl** option, which means that the surface complexation reactions do not consider any electric double layer effects.

Using the **no_edl** mode, no input is required for surface area and sorbent mass. It is important to note, that the unit of surface site density is moles of sites per litre of solution. Each individual laboratory batch sorption experiment is simulated in PHREEQC as a batch reaction between the **SURFACE** and an aqueous **SOLUTION** for which the composition is changed from experiment to experiment. *As(III)* and *PO₄* were added using the **REACTION** keyword while the naturally adsorbed concentrations of *As(III)* and *PO₄* were included in the initial solution using the **SOLUTION** and **SOLUTION_SPREAD** keywords. The experimentally observed pH was fixed in the model using the **EQUILIBRIUM_PHASES** keyword:

EQUILIBRIUM_PHASES 1
Fix_pH -6.30 HCl 10.0

where, **Fix_pH** is defined in the **DATABASE** section of the model file as follows:

PHASES
Fix_pH
H+ = H+
log_k 0

Finally, the **USER_GRAPH** keyword is used to control the simultaneous plotting of the observation data and of simulation results. You can now play with this model and systematically vary the values of two selected adjustable model parameters, i.e.,

- one of the three logKs for *As(III)* (Hint: try logKs between 40 and 45)
- surface site density for *Site_sOH* (Hint: try densities between 1×10^{-5} and 3×10^{-5})

Fill the values that achieve the best match with the observed data into Table 5.7 .

5.6 PHT3D Exercise 7: Incorporation of the site-specific SCM into a reactive transport model

At the study site for which the above SCM was developed, Van Phuc, groundwater extraction near Hanoi and the resulting changes in hydraulic conditions have caused surface water from the Red River to infiltrate into the adjacent Holocene aquifer and further into the laterally neighbouring Pleistocene aquifer. Associated with the changes in hydrological conditions arsenic mobilisation at the interface between the Red River and the aquifer has caused an extensive arsenic plume at the site. However, while the mobility of As in the Holocene aquifer is considered to be relatively high, As transport within the Pleistocene section of the aquifer has been significantly retarded (van Geen et al., 2013). In this PHT3D exercise we use a simple 1-D reactive transport model to illustrate the effect of variable geochemical conditions on the extent of As sorption, most importantly how competition between PO_4 and As affects arsenic mobility. We will compare how the effective retardation factors that are obtained with these SCM-based models compared coefficients compare with the earlier suggested retardation factors of 16 to 20 (van Geen et al., 2013).

For this exercise the model file [as_1d.orti](#) and the corresponding database file [pht3d_datab.dat](#) are provided as a base version. The model simulates groundwater flow over a 50-year period over a distance of 2,500 m. The conservative transport behaviour of the model can be seen from visualising the concentration of the species **Tracer** in the Transport Results section. This can be done by

- going to [Parameters](#) → [3. Transport](#) → [Spc](#), specifying [Type](#) → [Mt3dms](#) and entering the word **Tracer** under [Species](#).
- Then under [Parameters](#) → [3. Transport](#) → [P](#), select [RCT](#) → [rct.1](#) → [major flags](#) and enter [ISOTHM sorption](#) → no sorption.
- Now that we have defined a conservative tracer species, we will provide its concentration in [Spatial Attributes](#) → [Mt3dms](#) → [BTN](#) → [btn.13 Concentrations](#).
- Use the point zone tool to add a tracer concentration of 1 in the 1st grid cell ($x = 1.2\text{m}$, $y = 0.5\text{m}$). Set the background boundary condition type to 1 in all grid cells. To do this go to [Spatial Attributes](#) → [Mt3dms](#) → [BTN](#) → [btn.12](#). Boundary conditions → [Backg..](#)
- Now write the model input files and run MT3DMS.

- You can now visualise the concentration profile of the tracer for the final time step (18250 days) under [Results](#) → [3. Tracer](#).

In a first step we will reproduce the results of van Geen et al. (2013) by employing a linear sorption model for *As* such that the proposed retardation factor of 16 is achieved.

- Go to [Parameters](#) → [3. Transport](#) → [Spc](#), specify [Type](#) → [PHT3D](#) and enter [Species](#) → *As_three*.
- Then under [Parameters](#) → [3. Transport](#) → [P](#), select [RCT](#) → [rct.1](#) → [major flags](#) and enter [ISOTHM: sorption](#) → [linear](#).
- Now, in [Parameters](#) → [3. Transport](#) → [Ret](#), enter a value of 1.7 for [SP1](#), which represents the distribution coefficient *K_d*.
- Then, under [Spatial Attributes](#) → [Mt3dms](#) → [RCT](#) → [rct.2a bulk density](#) provide a [Background](#) value of 1.988 kg/l for all cells.
- Now go to [Parameters](#) → [4. Chemistry](#) and [import database](#) and then enter into Chemistry tab.
- You can see that different solution compositions have already been entered for you. Under [Spatial Attributes](#) → [Pht3d](#) → [ph.3 Initial chemistry](#) specify the [background](#) solution 0 and under [ph.4 Source/sink](#) use [add zone](#) to specify a source concentration for solution 1 in the 1st grid cell.
- Write the model input files and run PHT3D.
- Once the model execution is finished you can visualise the profile of *As_three* at time 18250 days under [Results](#) → [5. Observations](#). Similarly, you can reproduce a retardation factor of 20 by changing the [SP1](#) value to 2.1 l/kg.
- Finally, to incorporate surface complexation model in the 1-D simulation, de-activate the [RCT](#) module of MT3DMS and specify the surface site density values for [Site_s](#) under [Parameters](#) → [4. Chemistry](#) → [Surface](#) → [Site_back](#). Now write the model input files and run PHT3D. Then compare the *As_three* concentration profile with the profile obtained with the linear isotherm simulations.

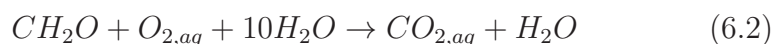
What is the resulting retardation factor for *As* in the SCM-based model ?

Chapter 6

Redox Reactions

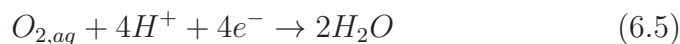
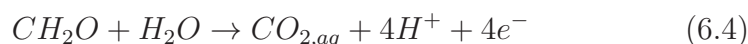
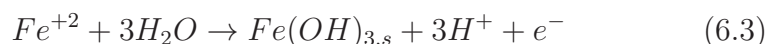
6.1 Background

Understanding oxidation-reduction (redox) reactions that occur in natural and contaminated systems is central to developing accurate conceptual and quantitative models. Redox reactions involve the transfer of electrons between constituents and therefore, changes in the oxidation state of one or more elements. Changes in oxidation state of an element can result in dramatic changes in its chemical and physical properties. For example, iron in the plus three oxidation state - Fe(III) - in surficial deposits renders a reddish hue to Mars whereas iron in the plus II oxidation state - Fe(II) - in surficial basalts on the Moon is, in no small part, responsible for the blackness of the lunar maria. Two important examples of redox reactions are the oxidation of aqueous Fe(II) to Fe(III) or organic carbon by dissolved oxygen:



Rather than representing formaldehyde, CH_2O is often used to represent one sixth of a glucose molecule.

The classical approach to discussing redox reactions in aqueous geochemistry is to split the redox reactions into two hypothetical half reactions involving electrons. Using this approach, reaction 6.1 and 6.2 would be broken up into the following half reactions:



Mass action expressions are then written for the half reactions. For example, for the Fe(II)/Fe(III) half reaction, the mass action expression is:

$$K = a_{Fe(OH)_{3,s}} a_{H^+}^3 a_{e^-} / a_{Fe^{+2}}^2 a_{H_2O}^3 \quad (6.6)$$

The standard state of the e^- is the same as other aqueous species, 1 mole per kilogram water. This approach comes from the field of electrochemistry, where the oxidation and reduction half reactions can be made to occur in separate place connected, for example, through a meter that measures the electromotive force (or power source) and a salt bridge. In dilute solutions the activity of water can be equated with its mole fraction, which is essentially 1. If pure ferric hydroxide forms then it can be assumed to be in its standard state (mole fraction $Fe(OH)_{3,s}$ equals 1), so ?? can be re-written:

$$K = a_{H^+}^3 a_{e^-} / a_{Fe^{+2}}^2 \quad (6.7)$$

Taking the base-10 logarithm, 6.7 becomes:

$$\log K = 3 \log a_{H^+} + \log a_{e^-} - 2 \log a_{Fe^{+2}} \quad (6.8)$$

Analogous to the definition of pH , $\log a_{e^-}$ is defined as pe . This formalism is useful for graphically representing the relative thermodynamic stability of redox-reactive species in natural and contaminated systems (typically in their standard state).

Electrochemists have established $\log K$ values for half reactions based on the convention that the hydrogen gas - hydrogen ion half reaction



has an electromotive force and, therefore a $\log K$ value of 0 for $H_{2,g}$ and H^+ in their standard states (1 atmosphere and 1 mol/kgw, respectively). Using this convention, $\log K$ values for half reactions can be assembled in order of thermodynamic favorability, called a redox ladder, such as Table 6.1. Note that the $\log K$ values apply to all species in their standard state (1 mol/kgw for aqueous species, pure solid phase activity equals 1, and 1 atmosphere for gasses). Also, the $\log K$ value for half reactions where solid phases are participants depends on the thermodynamic stability of the solid phase. For example, reduction of ferrihydrite (fhy) is more favorable than reduction of goethite (based on the $\log K$ values for goethite that applies to the Cape Cod aquifer, Kent et al., 2008) because goethite is thermodynamically more stable than ferrihydrite. Plots of pH against pe constructed using reactions and $\log K$ values like those in Table 6.1 are used to illustrate trends

expected in redox processes with changes in pH. In the exercise that follows, we will explore these trends.

Table 6.1: Half reactions and logK values for some redox-reactive species

Half reactions, per electron	logK
$0.25\text{O}_{2,\text{aq}} + \text{e}^- + \text{H}^+ = 0.5\text{H}_2\text{O}$	21.52
$0.2\text{NO}_3^- + \text{e}^- + 1.2\text{H}^+ = 0.1\text{N}_2,\text{aq} + 0.6\text{H}_2\text{O}$	20.71
$0.5\text{MnO}_2:\text{H}_2\text{O}_s, \text{pyrolucite} + \text{e}^- + 2\text{H}^+ = 0.5\text{Mn}^{+2} + 1.5\text{H}_2\text{O}$	20.69
$0.5\text{HAsO}_4^{2-} + \text{e}^- + 2\text{H}^+ = 0.5\text{As}(\text{OH})_3,\text{aq} + 0.5\text{H}_2\text{O}$	19.80
$\text{FeOOH} + \text{e}^- + 3\text{H}^+ = \text{Fe}^{+2} + 2\text{H}_2\text{O}$	fly 17.91
$\text{FeOOH} + \text{e}^- + 3\text{H}^+ = \text{Fe}^{+2} + 2\text{H}_2\text{O}$	Goethite (Kent et al. 2008) 13.52
$0.125\text{SO}_4^{2-} + \text{e}^- + 1.125\text{H}^+ = 0.125\text{HS}^- + 0.5\text{H}_2\text{O}$	4.21
$0.125\text{CO}_3^{2-} + 1.25\text{H}^+ + \text{e}^- = 0.125\text{CH}_4,\text{aq} + 0.375\text{H}_2\text{O}$	5.13

6.2 PHREEQC Exercise 6

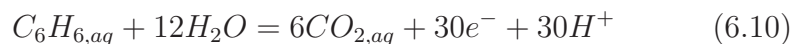
In this exercise we will examine the influence of chemical composition on redox processes and feedback between redox reactions and chemical composition.

Consider the half reactions listed in Table 6.1. Based on these half reaction fill in column two of 6.2. Enter the ratio of H^+ produced per e^- consumed. Use positive numbers where H^+ is produced by the consumption of electrons and negative numbers where H^+ is consumed by the consumption of electrons. This is, of course, not the conventional way of calculating stoichiometry, but what we are after is whether the redox process should decrease the pH (produce H^+), increase the pH (consume H^+), or have no impact on pH.

Table 6.2: H^+ stoichiometry of redox reactions.

Redox Couple	H^+/e^-	$\text{H}^+/\text{C}_6\text{H}_6$
$\text{O}_{2,\text{aq}}/\text{H}_2\text{O}$		
$\text{NO}_3^-/\text{N}_{2,\text{aq}}$		
$\text{MnO}_2\text{H}_2\text{O}_s/\text{Mn}^{+2}$		
$\text{H}_2\text{AsO}_4^-/\text{As}(\text{OH})_3,\text{aq}$		
$\text{FeOOH}_{s,\text{fly}}/\text{Fe}^{+2}$		
$\text{FeOOH}_{s,\text{gte}}/\text{Fe}^{+2}$		
$\text{SO}_4^{2-}/\text{CO}_{2,\text{aq}}$		
$\text{CO}_3^{2-}/\text{CH}_{4,\text{aq}}$		

Now, consider the half reaction where benzene is oxidized to $\text{CO}_{2,\text{aq}}$:



The $\log K$ for this reaction is uncertain but we will assume that conversion of benzene to either CO_2 or methane is favorable. Combining this half reaction with each of the reactions in Table 6.1 to eliminate e^- produces the following overall reactions for the oxidation of benzene by each of the oxidants. Using the reactions in Table 6.3, fill in column three of Table 6.2

Table 6.3: Overall reactions for the oxidation of benzene by the

Overall reaction		
$15O_{2,aq} + 2C_6H_{6,aq} + 6H_2O$	$=$	$12CO_{2,aq} + 6H_2O = 12HCO_3^- + 12H^+$
$6NO_3^- + C_6H_{6,aq} + 6H^+$	$=$	$3N_{2,aq} + 6CO_{2,aq} + 6H_2O$
$15MnO_2H_2O_s + C_6H_{6,aq} + 30H^+$	$=$	$15Mn^{+2} + 6CO_{2,aq} + 33H_2O$
$15H_2AsO_4^- + C_6H_{6,aq} + 15H^+$	$=$	$15As(OH)_{3,aq} + 3H_2O + 6CO_{2,aq}$
$30FeOOH_{s,fhy} + C_6H_{6,aq} + 60H^+$	$=$	$30Fe^{+2} + 48H_2O + 6CO_{2,aq}$
$30FeOOH_{s,gte} + C_6H_{6,aq} + 60H^+$	$=$	$30Fe^{+2} + 48H_2O + 6CO_{2,aq}$
$15SO_4^{-2} + 4C_6H_{6,aq} + 15H^+$	$=$	$24CO_{2,aq} + 15HS^- + 12H_2O$
$4C_6H_{6,aq} + 18H_2O$	$=$	$15CH_{4,aq} + 9CO_{2,aq}$

- For which reactions are there qualitative changes in the H^+ stoichiometry (influence of pH) when the overall reaction is considered as compared to the half reaction ?
- What quantitative differences are there in the H^+ stoichiometry between Fe(III) reduction and sulfate reduction when the overall reaction is considered as compared to the half reaction ?
Fe(III) reduction and methanogenesis ?
- Calculate the number of umoles of C_6H_6 required to deplete each of the electron acceptors. Record the number of umoles of C_6H_6 to the tenths place and then tabulate the running total in Table 6.4. You will use the running total in the PHREEQC exercise that follows.

Table 6.4: Hand-calculation table. EA refers electron acceptor.

EA	Initial μ moles	μ moles C_6H_6 to deplete EA	Total μ moles C_6H_6 added
O_2	250		
NO_3^-	1500		
$MnO_{2,s}$	800		
$As(V)$	0.55		
$FeOOH_s$	8000		
SO_4^{-2}	260		

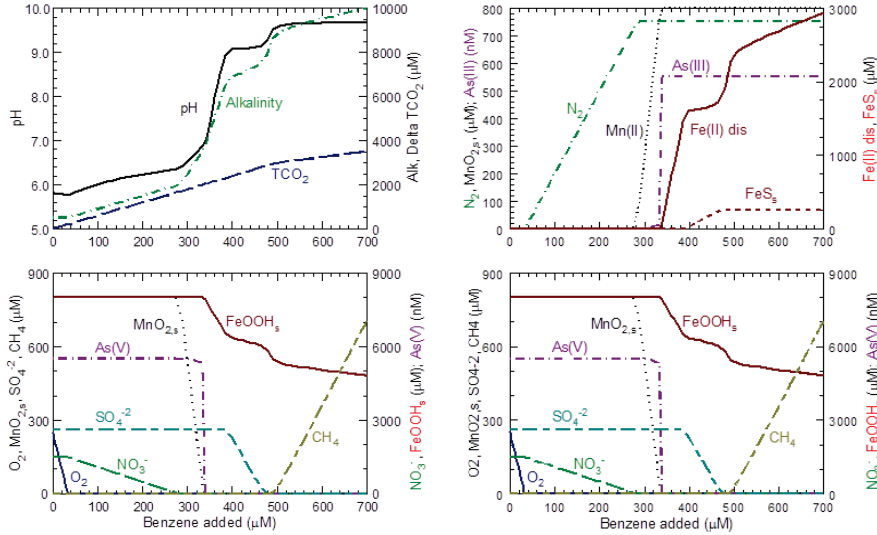


Figure 6.1: Results of the redox titration simulation.

Now we will use PHREEQC to conduct a redox titration (Abrams et al., 1996; Appelo and Postma, 2005). Small increments of benzene will be added to a suspension with one kilogram of water whose initial composition is listed in [redox_titration.phrq](#). Based on the composition and thermodynamic data already described, in what order do you expect the electron acceptors to be completely reduced by benzene?

We will use the PHREEQC file [redox_titration.phrq](#) which adds benzene in a series of steps pre-determined to make the model data plot up well. The results of the redox titration are shown in Figure 6.1.

In what order were the electron acceptors reduced?

How does this order differ from the order predicted by the redox ladder (Table 6.1)?

Why?

6.3 PHT3D Exercise 7: Artificial recharge and micropollutant fate

6.3.1 Background

Observed concentrations of reactive solutes in artificially recharged groundwater systems can often be highly dynamic and thus puzzling to interpret. For instance, concentration variations might be caused by effects, such as temperature variations, changes in groundwater flow rates, variations in the injected water quality, or a combination of those. One such example where the latter occurs is a study site in Berlin, Germany (Greskowiak et al., 2006), where aquifers are recharged by passing wastewater-impacted surface water through engineered infiltration ponds, as schematically illustrated in Figure 6.2. At this site, the temperature-dependent degradation of sediment-bound organic matter (SOM) was an important control for spatiotemporally varying oxygen concentrations. However, in addition, highly variable pond infiltration rates caused groundwater flow rates to change accordingly and to contribute further to the variability of the redox zonation. The model simulations focused initially on matching the data collected from in situ temperature loggers, and subsequently, the field-observed redox dynamics were replicated. In a final step, the degradation behavior of the micropollutant phenazone, a pharmaceutical residue, was investigated.

Through the model-based hypothesis testing and data interpretation it could be demonstrated that phenazone degraded in this system solely under aerobic aquifer conditions that dominated during winter. In contrast, phenazone remained persistent under the nitrate-reducing conditions that dominated during summer, while oxygen was depleted rapidly (Figure 6.2). Constraining the groundwater flow and solute transport processes prior to evaluating and calibrating the reactive processes associated with oxygen consumption allowed for residence time effects to be distinguished from temperature effects.

The hypothesized degradation behaviour was based on the results of various earlier laboratory experiments that have demonstrated that phenazone is biodegradable under oxic conditions (Zülke, 2004) in the presence of the aerobic bacterium *Phenyllobacterium immobile*. Batch experiments with sterilised and non-sterilised filter material suggest that aerobic microbial degradation is the most important removal process. Sorption of phenazone to filter material, sludge, or soil was found to be negligible. Importantly, it was also found that the degradation rate of phenazone is temperature-dependent, as its degradation, like that of organic matter, relies on microbial metabolism.

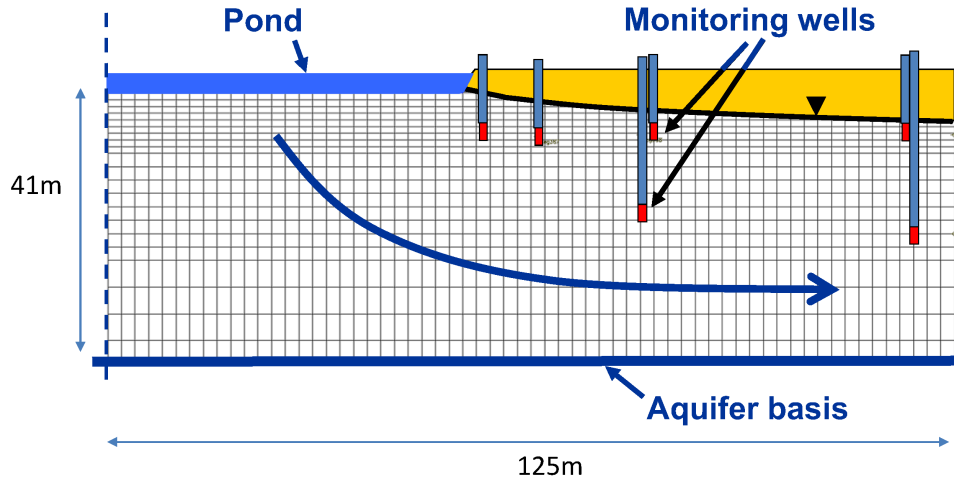


Figure 6.2: Schematic figure of the modelled infiltration pond transect

The model simulations in this exercise will employ and discuss the model approach that is described in more detail in Greskowiak et al. (2006). The type of redox-sensitive degradation behaviour that is illustrated in this exercise was previously also observed for many other micropollutants such as pesticides.

6.3.2 Governing kinetic reactions

The degradation rate r_{SOM} of the sediment-bound organic matter (SOM) that is present throughout the aquifer is simulated by a Michaelis-Menten type formulation:

$$r_{SOM} = f_T \left[r_{ox} \frac{C_{ox}}{K_{ox} + C_{ox}} + r_{nit} \frac{C_{nit}}{K_{nit} + C_{nit}} \frac{K_{ox,inh}}{K_{ox,inh} + C_{ox}} + r_m \right] \quad (6.11)$$

where f_T is an empirical function that describes the temperature dependent degradation of SOM. Thereby C_{ox} and C_{nitr} are the concentrations of dissolved oxygen and nitrate, respectively, r_{ox} , r_{nitr} , r_{mn} are the maximum rate constants under oxic, nitrate reducing and manganese reduction conditions, respectively, K_{ox} , K_{nitr} are the corresponding half-saturation constants, $K_{ox,inh}$ is the inhibition constant for nitrate reduction in the presence of oxygen. The degradation rate of phenazone is computed from:

$$r_{phena} = r_{phena,max} \frac{C_{ox}}{(k_{phena,ox} + C_{ox})} C_{phena} f_T \quad (6.12)$$

where $r_{phena,max}$ is the degradation rate constant, $k_{phena,ox}$ is the half-saturation concentration, and C_{phena} represents the concentration of phenazone.

The dependence of the reaction rate on the temperature T ($^{\circ}\text{C}$) is considered through the empirical function, f_T , as proposed by O'Connel (1995) and Kirschbaum (1995):

$$f_T = \exp(\alpha + \beta T(1 - 0.5 \frac{T}{T_{opt}})) \quad (6.13)$$

where α and β are fitting parameters and T_{opt} is the optimal temperature for the degradation reaction. T is the water temperature,

In the PHREEQC database the reaction rate expression for phenazone as used in Greskowiak et al. (2006) is formulated such that the reaction will only proceed in the presence of dissolved oxygen.

There are two parameters, i.e., [parm\(1\)](#) and [parm\(2\)](#) that can be modified within ORTI under the [Rates](#) Tab. If additional parameters should be edited, this can be achieved by editing the rate expression below accordingly.

```
#####  
Phenazone  
#####  
# from Greskowiak et al. 2006 (EST) -start  
7 mTmp = 1000 * tot("Tmp")  
10 Cphena = TOT("Phenazone")  
20 Cox = TOT("O(0)")  
26 a = -1.5;  
27 b = 0.18;  
28 Topt = 15  
30 fT = exp(a+b*mTmp*(1-0.5*mTmp/Topt))  
34 rph_max = parm(1)  
36 Khalf = parm(2)  
50 rate = fT* rph_max*(Cox/(Khalf+Cox)) * Cphena  
70 moles = rate * TIME  
200 save moles  
-end
```

The present exercise consists of three consecutive, increasingly complex stages:

- First we construct a steady-state flow and reactive transport model that simulates the fate of phenazone under constant temperature condition

- Subsequently we modify this model to study the impact of the field-observed dynamic temperature changes and associated with those, the temporal variations in the redox zonation
- Finally we also consider the highly variable infiltration rates and study how this affects the dynamics of the biogeochemical processes.

6.3.3 Steady flow model

To set up the steady state flow model

- Create a new model and set the model up as a [confined Xsection](#) model within the [modflow series](#).
- Set the geometry of the model domain with an extension in the x-direction from 0-125 m and in z-direction from 0-41 m. The grid discretization can be uniform with $dx = 6.25\text{m}$ and $dz = 4.1\text{m}$.
- To assist with the model construction, position a map of the cross section ([Background_image.png](#)) to use it as a background image during the model setup. To do this use the [Parameters](#) → [Model](#) → [Map](#) button
- The total simulation period considered is one year by going to [Parameters](#) → [Model](#) → [time](#) button and setting the maximum time to 360 days. Set the timestep length to 5 days, which will cause the model to force a reaction simulation every 5 days.
- Position a boundary condition for modflow ([bas.3](#)) at the right side (east) of the cross section from $z=0.25\text{m}$ to 33.25m . Add at the same location a fixed head ([bas.5](#)) boundary condition at $H = 35\text{ m}$. Set the head for the background at 40 m, this will be the starting head of the model.

The pond will be considered as a discrete recharge area, while the recharge in other areas can be neglected. In order to set this recharge area that represents the pond,

- Go into the [Addin menu](#) → [modflow modules](#) and select the [RCH](#) module. To see the module in the interface just click again on modflow.
- In this first phase of the exercise we will apply a steady recharge rate of 1.4 m/d under [RCH](#) → [rch.2](#) keep the background value at 0 and draw a horizontal line at the model top at the location

of the pond, i.e., from $x=0\text{m}$ to $x = 53\text{m}$, and provide a value of 1.4 (m/d) .

- As the infiltration rate is very high, we need to increase the number of internal time steps, in order to achieve an adequate numerical solution of the reactive transport problem. Click the [Parameter](#) Button under [Flow](#) and chose [DIS](#) → [dis.8](#) and change the [NSTP](#) value to 2. This results in 2 time steps within each stress period.
- Set the hydraulic conductivity to 50 m/d by going to [LPF](#) → [lpf.8](#) and writing 50 in the background box before clicking [ok](#). This will apply to the whole model.
- The vertical hydraulic conductivity is set by defining a ratio for K_h/K_v . To do this go first to [Flow](#) → [Parameters](#) → [LPF](#) → [lpf.5](#) and set the value to a ratio k_h/k_v . Then in [Spatial attributes](#) → [modflow](#) → [lpf.9](#) set the value of the ratio of 1 for the whole model (use the background value)
- Now run MODFLOW.

6.3.4 Steady flow, chemistry and constant temperature

To integrate the reactive transport processes into our model

- You will first specify the advection scheme that will be used. We will select the MOC scheme in [Parameters](#) → [Transport](#) → [Parameters](#) → [ADV](#) → [adv.1 global](#).
- Subsequently the dispersivity is defined under [Spatial attributes](#) → [mt3dms](#) → [dsp.2](#) for the longitudinal dispersion, where we will keep the default value of 1 m.
- Furthermore, we will also leave the ratio of the vertical to the longitudinal dispersivity at 0.05.
- The porosity (0.35) is set in the [Spatial attributes](#) → [mt3dms](#) → [btn.11](#) → [porosity](#).
- Import the `pht3d_datab.dat` via the import button under Chemistry. You will get a long list of aqueous components under ([Add_Chemistry](#) Button → [Solutions](#)). However, we will need to activate only a few of those.

- Check the file [Berlin_data_for_model.xls](#) sheet stage 1. Copy the species values for the [Backgrd](#) and the [Solul](#) column from the spreadsheet into the corresponding columns of the ORTi3D interface. Check the values, and click those active where at least one value of the [Backgrd](#) and [Solul](#) is non-zero.
- Note that for numerical reasons the species Tmp carrying the Temperature is given in milli °C.
- Under [Rates](#), all [RATES](#) are imported from the [pht3d_datab.dat](#) database. Select only [Orgc_sed](#) and [Phenazone](#). Also, select [Orgc_sed](#) to act as an immobile (IM) species to reflect the fact that this organic matter is attached to sediments.

The [Orgc_sed](#) species is here not really meant as the concentration of sedimentary organic matter. Rather, it is used in here as a reactivity parameter that defines the overall reactivity of the organic matter in the aquifer, and linked to the consumption of terminal electron acceptors via [RATES](#) in the database. It was assumed that there is always a sufficient amount of degradable organic matter such that it does not become rate-limiting. The parameters [parm1](#) to [parm5](#) correspond to the parameters that are used in the database.

All kinetic reaction and temperature parameters are given in Table 6.6. Note that the constants T_{opt} , α and β were hard-coded in the [pht3d_database.dat](#) database and don't need to be specified via the ORTi3D user interface.

- For the rate [Orgc_sed](#) the stoichiometry of the reactive constituents associated with the reaction has to be entered under formula: Enter [CH2O 1 NH3 0.15](#).
- Subsequently enter the formula [Phenazone -1](#) to be associated with the rate of [Phenazone](#) degradation.
- Go to [Phases](#) and click [Calcite](#) and provide a background concentration under [Backg_Moles](#) of 1.7 and for [Pyrolusite](#) add a

Table 6.5: Reaction parameters in the included reaction rate expressions.

	Parm(1)	Parm(2)	Parm(3)	Parm(4)	Parm(5)
SOM / Org_sed	r_{ox}	$K_{ox} = K_{ox,inh}$	r_{nitr}	K_{nitr}	r_{mn}
Phenazone	$r_{phena,max}$	$K_{phena,ox}$			

concentration of 3e-3 under [Backg.moles](#) and similarly enter 0 for [Rhodochrosite](#).

- Now we have to assign the aqueous solutions that will act as initial and boundary conditions in the model. Choose [Pht3d](#) → [PH](#) → [ph.3 Initial concentrations](#). Make sure that [Backg.](#) is set to 0, which means that solution 0 is used to define the initial water composition.
- Now choose [ph.5 Recharge](#). Define a zone that coincides with the infiltration area and enter solution number 1 into the right recharge box.
- Finally, everything is ready to run PHT3D.
- To visualise the simulation results of, for example, temperature, oxygen, nitrate and phenazone at monitoring wells, set observations zones [Spatial attributes](#) → [observation](#) → [obs.1](#) create lines that span the screened distance of the wells with well names. Then, in the panel [results](#) → [observation](#), select time series graphs and chemistry. In the dialog select the wells and then a layer (it can be any layer) and click twice on [Apply](#).
- To better compare the graphs, they may be exported and then the txt file can be opened in excel or further processed by python or matlab.

Table 6.6: Parameter values for kinetically controlled reactions

Parameter	Value	Unit
r_{ox}	1.32e-05	mol/L/d
$K_{ox} = K_{ox,inh}$	1.00e-05	mol/L
r_{nitr}	3.31e-06	mol/L/d
K_{nitr}	1.00e-05	mol/L
r_{mn}	7.70e-08	mol/L/d
$r_{phena,max}$	12	1/d
$K_{phena,ox}$	4.00e-04	mol/L
T_{opt}	35	°C
α	-1.5	-
β	0.18	1/°C

6.3.5 Seasonal temperature dynamics

- First, under [Chemistry](#) → [Parameters](#) → [PH](#) → [ph.6](#) → [specific options](#) and increase the [nb solutions](#) parameter to 12. This will allow to define 12 individual aqueous solutions (default is max 4).
- After that re-import the database file [pht3d_datab.dat](#).
- Under the [Ad_chemistry](#) feature, copy the composition from solution 1 ([solu1](#)) to solutions 2 ([solu2](#)) - solution 12 ([solu12](#)).
- Now you can enter or copy and paste the varying temperatures ([Tmp](#)) for [solu1](#) to [solu12](#). The values are provided in the Excel spreadsheet [Stage 2](#) (indicated in yellow) into the ORTi Interface to the species [Tmp](#).
- Now choose [ph.5 Recharge](#). Choose the zone for infiltration area, make it transient, and copy and paste the solution time series (time and solution number) given in Sheet [Stage 2](#) (marked in yellow, without the titles) into the right recharge box.
- Run PHT3D and study how the breakthrough curves at the observation wells have changed.

6.3.6 Temperature retardation due to heat exchange with the aquifer matrix

As now the temperature varies with time in the infiltration water, the generated temperature signal in the aquifer will be retarded due to heat exchange with the aquifer matrix. The retardation factor depends on the thermal characteristics of the porous medium is approximately $R = 2.1$ in the Berlin aquifer. This can be simulated with the [RCT](#) reaction package, specified under MT3DMS (this will automatically also assigned to PHT3D). To do so, we have to provide MT3DMS with the apparent density of the medium and the K_d to calculate the retardation factor R ($R = 1 + \rho_a * K_d / \text{porosity}$). With a porosity of 0.35 and a bulk density of 1722 kg/m³, this gives a K_d of 2.2e-4.

- To set these values you will have to add the [RCT](#) module to MT3DMS by (menu [Addin mt3dms modules](#)).
- then to go to the dialog [Parameters mt3dms](#) → [Parameters](#) → [RCT](#) → [rct.1](#) and set the sorption to linear.
- Once this is done go to [Spatial attributes](#) → [Mt3dms](#) → [Rct](#) → [rct.2a density](#) and set the value at 1722 for the background (i.e., everywhere).

- Then go to [Parameters](#) → [Transport](#) and click on [SPC](#), select [pht3d](#) in the choice box and write [Tmp](#) in the species box.
- After that, go to [Parameters](#) → [transport](#) → [Rct](#) and you will get a new dialog box with 4 parameters.
- Now enter a Kd value of 2.2e-4 in the [SP1](#) column.
- Re-run PHT3D

Inspect how this changes the time-concentration curves at the observation wells. You will notice that now the temperature breakthrough is slightly shifted towards later times, as the retardation of the heat transport also affects the redox system and thus ultimately also the phenazone breakthrough behaviour.

6.3.7 Stage 3: Seasonal temperature and infiltration dynamics

In this part of the exercise the recharge at the pond (infiltration rate) will be changed to a time-varying input to reflect the highly dynamic changes in infiltration rates that occurred at the field site. The 1-year long simulation period is therefore split into 12 monthly stress-periods. The employed rates are provided in the Excel spreadsheet [Stage 3](#).

- Select the two columns time and recharge (marked in yellow, without the titles) and copy them into ORTi to [RCH](#) → [rch.2](#), select the recharge zone and click on [value](#), which triggers the [zone dialog](#) to open. In this dialog select the [transient](#) option. A grid will appear in [values](#). Now paste the recharge values that you copied from the spreadsheet into this grid.
- Click the [Parameter](#) Button under [Flow](#) and select [DIS](#) → [dis.8](#) and change the simulation mode from [steady-state](#) to [transient](#) simulation.
- You now need to re-run MODFLOW. You can then check how the heads values and gradients are dynamically changing in the model.
- Finally re-run PHT3D and inspect how the transient recharge affected the breakthrough behaviour.

6.4 PHT3D Exercise 8: Reductive dissolution of Fe-oxides

Millions of humans worldwide are exposed to the consumption of ground-water contaminated with arsenic concentrations that exceed the World Health Organizations acceptable drinking water limit of 10 $\mu\text{g/L}$.

Arsenic occurs naturally in sediments, particularly in low-lying flood plain type environments with the most noteworthy occurrences in parts of Argentina, Bangladesh, Chile, China, Hungary, India, Mexico, Romania, Taiwan, and Vietnam. Understanding the coupled geochemical and hydrological processes that control arsenic mobility is vital for minimizing health impacts through the development of suitable mitigation strategies.

Under oxidising aquifer conditions, at circumneutral pH, arsenic generally does not pose a significant threat to groundwater resources because it strongly sorbs onto Fe-phases such as ferrihydrite or goethite. However, the intrusion of reactive organic carbon from sources such as carbon-rich sediments, constructed ponds, recent degradation of plants, and wastewater has in the meantime been identified as triggers for microbially mediated reductive dissolution of these iron phases, accompanied by the release of ferrous iron and trace elements such as arsenic.

This exercise illustrates the complex interplay of the key of geochemical processes that are involved in the release and transport of arsenic during the intrusion of (reactive) dissolved organic carbon into an aquifer that is initially characterised by low concentrations of dissolved arsenic. A more comprehensive discussion of modelling reductive dissolution of iron oxides and the associated fate of arsenic can be found, for example, in Rawson et al. (2016), who constrained their model development with the experimental data collected earlier by Tufano and Fendorf (2008) and in Rawson et al. (2017), which highlights the importance of multiple secondary reactions that were induced in parallel with the reductive dissolution of iron during a sucrose injection experiment.

6.4.1 Groundwater flow

In this exercise we use a pre-constructed model for groundwater flow and reactive transport while the focus of the exercise is to append the specific model input required to study iron mineral reactions and the fate of arsenic.

- In ORTI, load the copy of the numerical model that was readily prepared for this exercise. The groundwater flow in this verti-

cal transect model is induced by a steadily increasing hydraulic head gradient between the zone representing the interface with a river and the the model's downstream boundary. The modelled aquifer is characterised by two discrete aquifer zones of differing hydraulic conductivity. The upper, less permeable zone has a hydraulic conductivity of 5 m/day while the lower zone has a higher hydraulic conductivity of 40 m/day .

- Load the model file **as_river_base_model.orti** into ORTI.
- Inspect which aqueous species are included in the basic model.
- Run first MODFLOW and then PHT3D to inspect the results of this (effectively) non-reactive simulation.

6.4.2 Initiating redox reactions with dissolved electron acceptors

- Add degradable dissolved organic carbon (**Orgc**) as electron donor to the reaction network. Suitable reaction rate parameters for **Orgc** have already been entered for you.
- Add an **Orgc** concentration of 2×10^{-3} to the river water composition (**solu 1**).

6.4.3 Adding iron minerals to the reaction network

- Activate the iron mineral **Goethite**, **Siderite** and **FeS(ppt)** to the reaction network (under the **PHASES** Tab). To do so select Parameters → Chemistry → Phases and activate the species (tick the checkbox) for these minerals.
- Add a initial goethite concentration of $5 \times 10^{-3}\text{ mol/L}_{\text{bulk}}$. Assume that siderite and FeS(ppt) are not present at the beginning.

6.4.4 Arsenite sorption

So far the model contains only a small concentration of arsenite in the aqueous phase. In the next step the generic surface site **Site_s** will be added and the sorption site number will be linked to the amount of goethite that is present. As the amount of goethite can vary during the model simulation this will increase or decrease the number of sorption site accordingly. During reductive dissolution of iron this causes a steady loss of sorption capacity.

- Select Parameters → Chemistry → Surface and activate the species (tick the checkbox) **Site_s**
- Under Surface → Name add **Goethite** and under Surface → Switch add **equil** to the text box. This will tell PHT3D that the sorption site concentration will be proportional to the concentration of Goethite. Define the ratio *mol of sorption sites per mol of Goethite* where normally the initial concentrations for **Site_s** are defined. For this example enter 0.1 as the ratio of sorption sites per mass of goethite. Be careful to enter the value as concentration (second column) and not as a saturation index (first column).
- Adding the surface **Site_s** to the model will cause the equilibration of the aqueous solution with the surface. The concentrations of the surface complexes on the **Site_s** surface can be inspected by opening the file phout.dat, which is created by PHT3D during the model execution. After activation of the surface sites arsenite in the aquifer is initially mostly stored as sorbed arsenic.
- Rerun PHT3D and inspect the results.
- Check out how the **Orgc** plume evolves over time
- Check out the changes of the electron acceptors that participate in the degradation of **Orgc**, i.e., **O(0)**, **N(5)**, **S(6)** and **Goethite**
- Check how the arsenite plume evolves over time and try to explain the simulated behaviour.

6.5 PHT3D Exercise 9: Pyrite oxidation during deep well injection

6.5.1 Background

Managed aquifer recharge is increasingly used to enhance the sustainable development of water supplies. Common recharge techniques include aquifer storage and recovery (ASR), infiltration ponds, river bank filtration 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. Prommer and Stuyfzand (2005) 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 separate 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.

6.5.2 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

Table 6.7: Flow and transport parameters used for the deep well injection problem.

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

injection well.

- Use the data supplied in Table 6.7 to set up the flow model. Note 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). You can also visualise the heads along a profile that goes across the injection and extraction well by going to [Observation](#) → [OBS](#) → [obs.1 Observation](#) and defining a line.

6.6 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 background water 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 ?

6.6.1 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.

- Copy the reaction database that was developed for this problem into the folder where the ORTI model is located.
- Activate the relevant aqueous components that are needed to simulate the reactive transport of the chemicals listed in Table 1 of Prommer and Stuyfzand (2005). 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 ORTI Tab. Use the water composition as listed in Table 6.8. For the temperature **Tmp** enter a value of 0.017, which corresponds to 1/1000 of the temperature in Celcius. For pyrite use an initial concentration of 0.05 mol/l bulk volume and define it under the **Phase** Tab. 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.
- Define the water composition of the injected water as *Solution1*. Use the water composition measured at the 21 January 1997, as

listed in Table 6.8. For the temperature use a value of 0.0019 to represent a temperature of 1.9 C.

Table 6.8: Aqueous concentrations of the ambient groundwater and the injectant.

Aqueous component	C_{init} ($mol\ l_w^{-1}$)	C_{inject} ($mol\ l_w^{-1}$)
pH	6.68	7.1
pe	-2.45	13.5
Na	6.75×10^{-4}	1.26×10^{-3}
Cl	2.54×10^{-4}	1.82×10^{-3}
K	1.34×10^{-4}	1.23×10^{-4}
Ca	2.06×10^{-3}	1.87×10^{-3}
Mg	5.88×10^{-4}	3.25×10^{-4}
O(0)	0	8.13×10^{-4}
N(5)	0	3.54×10^{-4}
N(3)	0	0
N(0)	0	0
Amm	0	0
S(6)	5.52×10^{-5}	4.90×10^{-4}
S(-2)	0	0
Fe(2)	1.04×10^{-4}	0
Fe(3)	1.34×10^{-12}	2.68×10^{-7}
Si	2.81×10^{-4}	3.03×10^{-4}
C(4)	8.45×10^{-3}	3.14×10^{-3}
C(-4)	0	0
DOC	0	1.00×10^{-4}
Tmp	0.017	0.0019

- Attribute 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.
- Set a specified concentration boundary conditions at the left model boundary to define that the flux that occurs across this boundary has the same water composition as the ambient water.

To specify the water composition for this boundary select [Spatial Attributes](#) → [PHT3D](#) → [PH](#) → [ph.4 Source Sink](#) and define

a line along the boundary and set the *Zone Value* to the value representing the ambient water composition, i.e., to 0. Set the *Zone name* to *WQ_leftbound* or any other suitable name.

- Select the TVD scheme as advection package and define the dispersivities.
- Run the reactive transport model.
- Inspect the results by visualising 2D contours: Check how far did oxygen penetrate into the aquifer at the end of the simulation time ?
- Visualise the concentrations of **O(0)**, **N(5)** and **S(6)** at the extraction well by defining an observation well at the location of the extraction well. This can be done by selecting *Spatial Attributes* → *MODFLOW* → *Observation* → *OBS* → *obs.1 observation* and adding the observation location and defining a name for the observation point. Once the location is defined breakthrough curves can be visualised in the *Results* section.

6.7 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, ORTI allows to efficiently create multiple water compositions. to create the 12 different solutions that only differ with respect to their temperature allow first allow the model to have 12 solutions. To do so set in *PHT3D* → *PH* → *ph.6 specific options* set **NB_solu** to 12. After that re-import the database and open the chemistry dialog where you can now define up to 12 solutions. Then copy solution 1 to the next 11 (using ctrl+C and ctrl+v) and change the temperature to 8, 5, 9, 12, 15, 18, 22, 25, 21, 14, and 12, respectively.
- In final step of this part of the exercise the newly created temporally varying solutions (water compositions) have to be attributed to different stress-periods. This can be done by going to *Spatial Attributes* → *PHT3D* → *PH* → *ph.4 Source Sink* and by modifying the previously defined input that was created for a constant

injectant water composition to an input that will invoke a temporally (monthly) changing water composition. The numbers in the first column refer to the simulation time (simulation day nr) and the numbers in the second column refer to the number of the solution composition that will be used for the time period.

```
0 1
30 2
60 3
90 4
120 5
150 6
180 7
210 8
240 9
270 10
300 11
330 12
```

- Rerun the reactive transport model and inspect the oxygen and nitrate concentrations and how they vary with time and in space.

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 describe the relevant heat transport equation exactly. More details are described, for example, in Seibert et al. (2014).

6.8 Fate of a redox-sensitive micropollutant

In the next part of the exercise the fate of the pharmaceutical compound phenazone will be simulated and the impact of the seasonally changing redox zonation will be investigated.

Various laboratory experiments have demonstrated that phenazone is biodegradable under oxic conditions (Zülke, 2004) by the aerobic bacterium *Phenylobacterium immobile*. Batch experiments with sterilised and non-sterilised filter material suggest that aerobic microbial degradation is the most important removal process. Sorption of phenazone to filter material, sludge, or soil was found to be negligible. The simulations follow the model approach described in Greskowiak et al. (2006).

In the numerical model it was therefore assumed that phenazone degrades solely under aerobic conditions and that the degradation rate of phenazone depends on the dissolved oxygen concentration, a behaviour previously encountered with selected other micropollutants such as pesticides. It was also assumed that the degradation rate of phenazone is temperature-dependent, as its degradation, like that of organic matter, relies on microbial metabolism.

$$r_{phenazone} = r_{phenazone,max} \frac{C_{ox}}{(k_{phenazone,ox} + C_{ox})} C_{phenazone} f_T \quad (6.14)$$

where $r_{phenazone,max}$ is the degradation rate constant, $k_{phenazone,ox}$ is the half-saturation concentration, and $C_{phenazone}$ is the concentration of phenazone. The dependence of the reaction rate on the temperature T (°C) is considered through the empirical function, f_T , as proposed by O'Connell (1995) and Kirschbaum (1995):

$$f_T = \exp(\alpha + \beta T(1 - 0.5 \frac{T}{T_{opt}})) \quad (6.15)$$

where α and β are fitting parameters and T_{opt} is the optimal temperature for the degradation reaction. In the PHREEQC database the reaction rate expression for phenazone as used in Greskowiak et al. (2006) is formulated such that the reaction will only proceed in the presence of dissolved oxygen. There are two parameters, i.e., *parm(1)* and *parm(2)* that can be subsequently entered and/or varied within ORTI under the *Rates* Tab. If additional parameters should be edited this can be achieved by editing the rate expression below accordingly.

```
#####
Phenazone
#####
# from Greskowiak et al. 2006 (EST) -start
7 mTmp = 1000 * tot("Tmp")
10 Cphena = TOT("Phenazone")
20 Cox = TOT("O(0)")
26 a = -1.5;
27 b = 0.18;
28 Topt = 15
30 fT = exp(a+b*mTmp*(1-0.5*mTmp/Topt))
34 rph_max = parm(1)
36 Khalf = parm(2)
50 rate = fT* rph_max*(Cox/(Khalf+Cox)) * Cphena
70 moles = rate * TIME
```

```
200 save moles
-end
```

To include **Phenazone** take the following steps

- Activate the species **Phenazone** in the *Solutions* Tab. Enter an aqueous concentration of 1.0×10^{-6} mol/L for Phenazone for *Solutions* 1-12 but not for *Solution* 0, i.e., not for the background water composition.
- Define the reaction rate parameters for Phenazone under the *Rates* Tab. First, activate the Phenazone kinetics by ticking the first (C) box, but not the second (IM) box. The latter would make Phenazone an immobile species. Add a value of 5.0×10^{-6} for parm1 (reaction rate constant) and 4.0×10^{-4} for parm2. Finally add
Phenazone – 1.0 *C11H12N2O* 1.0 as *Formula*
 for phenazone to define the stoichiometry of the degradation reaction.

In the simulations of Greskowiak et al. (2006) it showed that the redox sensitivity (i.e., oxygen availability) dominated over the temperature effects on the phenazone degradation rates. In their study this behaviour resulted in significantly higher removal rates during the colder month of the year, when the aerobic zone of the aquifer was significantly larger.

A similar behaviour can also be seen if the breakthrough behaviour of phenazone is visualised at the extraction well.

6.9 Mobilization of arsenic

In the next 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 *Arsenopyrite* 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., $\text{parm}(1) = 0.001$ 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 activating the two surface species *Hfo_w* and *Hfo_s*. Then define the surface site densities for both of these species as 0.2 mol per mol of ferrihydrite and 0.005 mol per mol of ferrihydrite, respectively. Define those concentrations in the **Site_back** column in the **Surface**

Tab. Then add $Fe(OH)3(a)$ under the **name** column and **kinetic** under the **switch** column, both also in the **Surface** Tab. This will establish that the number of sorption sites is directly linked to the concentration of the (kinetically reacting) mineral phase $Fe(OH)3(a)$. Finally, define among the global PHT3D parameters that the **no_edl** option is used for the simulation. To do so set in **PHT3D** → **PH** → **ph.6 specific options** set **SU_OPT** to **no_edl**. This means that electric double layer calculations in the surface complexation model will be omitted.

- Run the model and inspect again the $As(5)$ and $As(3)$ breakthrough curves at the extraction well
- Compare the new results with the previous results (model run without surface complexation).

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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).
- 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, constant 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?