

3 Exercises

With the installation of the PHREEQC program, 18 examples are automatically installed in the folder “Examples”. They include:

Example 1.--Speciation calculation

Example 2.--Equilibration with pure phases

Example 3.--Mixing

Example 4.--Evaporation and homogeneous redox reactions

Example 5.--Irreversible reactions

Example 6.--Reaction-path calculations

Example 7.--Gas-phase calculations

Example 8.--Surface complexation

Example 9.--Kinetic oxidation of dissolved ferrous iron with oxygen

Example 10.--Aragonite-strontianite solid solution

Example 11.--Transport and cation exchange

Example 12.--Advective and diffusive flux of heat and solutes

Example 13.--1D transport in a dual porosity column with cation exchange

Example 14.--Advective transport, cation exchange, surface complexation, and mineral equilibria

Example 15.--1D Transport: Kinetic biodegradation, cell growth, and sorption

Example 16.--Inverse modeling of Sierra spring waters

Example 17.--Inverse modeling with evaporation

Example 18.--Inverse modeling of the Madison aquifer

A detailed description of the solutions for these examples can be found in the PHREEQC manual (Parkhurst & Appelo 1999). In addition, the following exercises for equilibrium reactions (chapter 3.1), kinetics (chapter 3.2) and transport (chapter 3.3) will help the user to become familiar with the possibilities and limitations of the program. The solutions of all exercises are explained in detail in chapter 4.

All exercises have been modeled with PHREEQC version 2.8.03. This latest version, available at the time of book printing, can be found on the enclosed CD (there are different versions of installation for Windows, Mac or Unix workstations).

3.1 Equilibrium reactions

3.1.1 Groundwater - Lithosphere

3.1.1.1 Standard-output well analysis

The following hydrogeochemical analysis (Table 29) is given for the drinking water well ("B3") in the model area shown in Fig. 40 (concentrations in mg/L):

Table 29 Hydrogeochemical analysis of the drinking water well B3 from Fig. 40

Temperature = 22.3°C	pH = 6.7	pE = 6.9	
Ca = 75.0	Mg = 40.0	K = 3.0	Na = 19.0
HCO ₃ ⁻ = 240.0	SO ₄ ²⁻ = 200.0	Cl ⁻ = 6.0	NO ₃ ⁻ = 1.5
NO ₂ ⁻ = 0.05	PO ₄ ³⁻ = 0.60	SiO ₂ = 21.59	F ⁻ = 1.30
Li = 0.030L	B = 0.030	Al = 0.056	Mn = 0.014
Fe = 0.067	Ni = 0.026	Cu = 0.078	Zn = 0.168
Cd = 0.0004	As = 0.005	Se = 0.006	Sr = 2.979
Ba = 0.065	Pb = 0.009	U = 0.003	

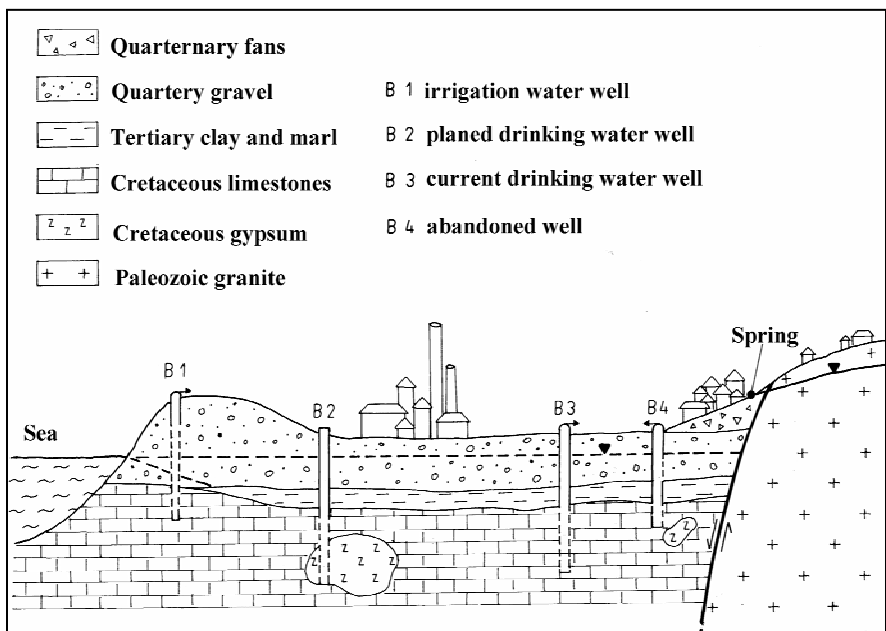


Fig. 40 Model area for exercises in the chapters 3.1.1.1 - 3.1.1.8, chapter 3.1.4.1, chapter 3.1.4.3, chapters 3.1.5.2 - 3.1.5.5

How would you interpret the analysis? Have a close look at the redox sensitive elements (which elements do not fit in the general scheme and why?). Present the species distribution of the Ca-, Mg-, Pb- and Zn-species in the form of a pie chart

(what is remarkable?). Illustrate the supersaturated Fe- and Al-mineral phases by means of two bar charts.

3.1.1.2 Equilibrium reaction - solubility of gypsum

The town council plans to drill a new well for drinking water supply. From a logistic point of view (lengths of water pipes), it should be closer to the town than the present drinking water well B3. The new, planned location can be found as “B2” in Fig. 40. Is the planned location advisable from a hydrogeochemical point of view? Assume that the general direction of groundwater flow is from the East to the West. Furthermore, regard the analysis of the drinking water well B3 as characteristic for the aquifer east of the B2. Point out changes in the water chemistry and take into account drinking water standards when drawing a final conclusion.

3.1.1.3 Disequilibrium reaction - solubility of gypsum

How does the water quality change when assuming that the retention times in the underground are so short that only a 50 %-saturation with regard to the predominant mineral phase will occur? (*Note: Using the key word EQUILIBRIUM_PHASES, it is not only possible to specify equilibria, but to determine defined disequilibria with the help of the saturation index as well. A saturation of 80% (undersaturation) would mean e.g.: $IAP/KT = 80\% = 0.8$; $\log IAP/KT = SI = \log 0.8 \approx -0.1$; see also Eq.35).*)

3.1.1.4 Temperature dependency of gypsum solubility in well water

Data of more recent drilling holes show a certain geothermal influence in the area of B2. How would different temperatures in the underground affect the water quality in the planned well B2 (simulation range 10, 20, 30, 40, 50, 60, 70°C with a saturation of 50 %)? [*key word REACTION_TEMPERATURE*]

3.1.1.5 Temperature dependency of gypsum solubility in distilled water

Only for comparison: How much gypsum will be solved in distilled water at the same temperatures? How can the difference be explained in comparison to the well water?

3.1.1.6 Temperature and $P(\text{CO}_2)$ dependent calcite solubility

In the well B3, seasonally changing amounts of calcium have been measured. This phenomenon is ascribed to karst weathering, which is not only dependent on

temperature but also on the CO₂ partial pressure in the soil (often increased CO₂ concentrations in the soil are a product of microbial decomposition reactions). Simulate the theoretical solubility of calcite for a whole year with temperatures on winter days of 0 °C and a low CO₂ partial pressure (corresponding to the value of the atmosphere) up to temperatures of 40 °C and a high bioproductivity (P(CO₂) = 10 Vol%) during summer times.

The following pairs of temperature and CO₂ partial pressure are given:

Temp.(°C)	0	5	8	15	25	30	40
CO ₂ (Vol%)	0.03	0.5	0.9	2	4.5	7	10

Where is the maximum of karst weathering (tabular and graphic illustration) and why?

[*Note: Gas phases can be put into equilibrium like mineral phases. Instead of SI use the gas partial pressure p : Convert CO₂ Vol% into [bar] and form the logarithm; e.g. 3 Vol% = 0.03 bar = -1.523 P(CO₂).]*

3.1.1.7 Calcite precipitation and dolomite dissolution

What happens when not only pure calcium carbonate (calcite) but also magnesium calcium carbonate (dolomite) exists? Present your results graphically. How is this kind of reaction called? [*For simulation use mineral phase dolomite(d) = dispersive distributed dolomite*]

3.1.1.8 Calcite solubility in an open and a closed system

While simulating the two previous exercises 3.1.1.6 and 3.1.1.7 you always assumed that the amount of CO₂ was unlimited. Such systems are called “open systems”. In reality, this is very rare. Usually, there is only a restrained amount of gas available (closed system).

Simulate for the drinking water well B3 the solution of calcite for an open and a closed system using a temperature of 15 °C and partial pressures of 2 and 20 Vol% respectively. Where is the difference between the two systems? What changes with increasing partial pressure and why? Consider, besides the solution of calcite, changes in pH values, too.

[*Note: closed system: key word GAS_PHASE; here, the following parameters have to be defined: the total pressure = 1 bar, the volume = 1 L gas per L water, and the temperature of the gas = 35 °C; additionally: which gas is being used (CO₂) and which partial pressure exists (here not the log P(CO₂) is used like in EQUILIBRIUM_PHASES, but the CO₂ partial pressure in bars!]*

3.1.1.9 Pyrite weathering

Many reactions are so slow that it is impossible to describe them using equilibrium reactions (e.g. the weathering of quartz, or pyrite in the absence of microorganisms). However, it is often interesting to figure out to what extent these

slow transformations affect the pH value or other (equilibrium) reactions in solution. Therefore, transformations are experimentally modeled to find out possible relations between the amount of reaction products and the time from sections of linear correlations.

When flooding an abandoned mine processes of oxidation and reduction are of great importance. Due to the supply of oxygen, protons and sulfate are formed changing the chemistry of ground water fundamentally, e.g. mobilisation of metals as a result of the decrease of the pH value (“acidification”).

Model the oxidation of pyrite with different oxygen supplies (0.0, 0.001, 0.005, 0.01, 0.05, 0.1, 0.3, 0.6, 1.0 mol), and show the changes graphically for the two major elements building up from pyrite dissolution as well as for the pH value of the ground water given in Table 30.

Table 30 Water analysis of a ground water (concentrations in mg/L).

pH	6.5		
Redox potential	-120 mV	Al	0.26
Temperature	10.7 °C	SiO ₂	24.68
O ₂	0.49	Cl	12.76
Ca	64.13	HCO ₃	259.93
Mg	12.16	SO ₄	16.67
Na	20.55	H ₂ S	2.33
K	2.69	NO ₃	14.67
Fe	0.248	NH ₄	0.35
Mn	0.06	NO ₂	0.001

[Note: The key word for the addition of definite amounts of a reactant to a solution is REACTION. The command SELECTED_OUTPUT, which has already been mentioned in chapter 2.2.1.4, is very useful here. It directly displays all required data in an extra file in a spreadsheet format, so the user does not have to look through the whole output manually. Under “molalities” and under “totals” the species of interest and the total concentration of an element can be issued, respectively.

In the data set used so far (WATEQ4F), NH₄ is not included. Therefore, it has to be defined as an additional species. It can be done either directly in the data set or – like in this example – in the input file (see chapter 2.2.1.1). For that, NH₄ has to be defined as a species and a respective reaction equation has to be included. The key words are the same as for their definition in the data set:

SOLUTION MASTER SPECIES

N(-3) NH₄ 0.0 14.0067

SOLUTION_SPECIES

#NH₄ secondary master species 127

NO₃⁻ + 10H + 8e⁻ = NH₄⁺ + 3 H₂O

log₁₀ k 119.077

delta h -187.055 kcal

Anything in the input file always overwrites information in the database. Thus, NH_4 can be defined as a species only for this exercise without changing the whole WATEQ4F data set and without having problems with regard to the maintenance of the data set, the verification of the consistency of the data sets, the existence of the products, and the differences in the conditions under which the solubility constants as well as the absolute values have been determined (see also chapter 2.1.4.1 and chapter 2.1.4.2).]

Additionally, show if it is possible to attenuate the reactions when adding calcium carbonate. Add $\text{U}_3\text{O}_8(\text{c})$ as a mineral phase and test if a diminution in the concentration of uranium can be observed when adding calcium carbonate.

[It is worthwhile remarking that a lot of these slow reactions do not proceed linearly and therefore they can only be modeled to a first approximation. The weathering of pyrite, e.g., will be catalyzed by microbes which are subject to exponential growth and death. These kinetics are taken into consideration in chapter 3.2.1.]

3.1.2 Atmosphere – Groundwater – Lithosphere

3.1.2.1 Precipitation under the influence of soil CO_2

Considerable amounts of carbon dioxide are produced in the soil as a result of microbial degradation reactions. Particularly during the summer, concentrations of CO_2 soil gas of approximately 1-5 Vol% can be reached under humid climate. This amount is a significant increase compared to CO_2 partial pressures in the atmosphere of 0.03 Vol% (see also the exercise in chapter 3.1.1.6). Simulate the effect that a soil CO_2 partial pressure of 1 Vol% has on the following rainwater: Na = 8, K = 7, Ca = 90, Mg = 29, SO_4^{2-} = 82, NO_3^- = 80, C(+4) = 13 and Cl = 23 [all units in $\mu\text{mol/L}$]. Value of pH: 5.1, temperature: 21°C.

Attention: In PHREEQC, C(+4) has indeed to be expressed as C(+4) and not as alkalinity as we did it so far. Because of the low concentrations in rainwater, a “conventional” determination of the alkalinity is not possible, only the determination of the TIC (total inorganic carbon, C(+4)) can be done.

3.1.2.2 Buffering systems in the soil

How do the different buffer systems in the soil (Al-hydroxide-, exchanger- (50 % NaX, 30 % CaX_2 , 20 % MgX_2), carbonate-, Fe-hydroxide-, Mn-hydroxide buffer) affect the chemical composition of the rainwater of the previous exercise (chapter 3.1.2.1) when it infiltrates in the soil (CO_2 partial pressure 1 Vol%)?

[For modeling the exchanger buffer use the key word EXCHANGE and then define the exchanger species and their respective amounts (e.g. NaX 0.5).]

3.1.2.3 Mineral precipitates at hot sulfur springs

The following analysis of a sulfur-rich thermal water is given (Table 31):

Table 31 Water analysis of a sulfur-rich thermal water (concentration in mol/L)

pH	4.317	pe	-1.407	Temperature	75°C
B	2.506e-03	Ba	8.768e-08	C	1.328e-02
Ca	7.987e-04	Cl	5.024e-02	Cs	9.438e-06
K	3.696e-03	Li	1.193e-03	Mg	2.064e-06
Na	4.509e-02	Rb	1.620e-05	S	8.660e-03
Si	7.299e-03	Sr	3.550e-06		

Model what happens when this water discharges at a spring outlet and comes into contact with atmospheric oxygen and CO₂. Take into account that the diffusion of gas in water proceeds relatively quickly but that the contact with oxygen results in redox reactions which much slower kinetics. Therefore, restrict the addition of oxygen with the help of the command REACTION from 1 mg O₂/L to the maximum amount of O₂ that can be dissolved assuming that the water close to the spring cools down to 45 °C (gas solubility decreases with increasing temperature, see chapter 1.1.3.1).

[Hint: Table 32 presents the O₂ gas solubility in cm³ per cm³ water at a partial pressure of 100 Vol%]:

Table 32 Dependence of O₂ solubility on temperature at P(O₂) = 100 %

Temperature	Gas solubility	Temperature	Gas solubility	Temperature	Gas solubility
0	0.0473	20	0.0300	50	0.0204
5	0.0415	25	0.0275	60	0.0190
10	0.0368	30	0.0250	70	0.0181
15	0.0330	40	0.0225	90	0.0172

Estimate from Table 32 how much O₂ per liter water is dissolved at the given temperature and at an atmospheric O₂ partial pressure. For this approximation it can further be assumed that there is 1 mole O₂ in 22.4 liter gas.]

3.1.2.4 Formation of stalactites in karst caves

The rainwater of exercise chapter 3.1.2.1 infiltrates in a karst area. There is enough time that an equilibrium regarding the predominant mineral phase and an elevated CO₂ partial pressure of 3 Vol% can be reached.

In the underground, there is a karst cavern with an extension of 10 m length, 10 m width and 3 m height connected via a natural tunnel to the atmosphere. Approximately 100 liter of the infiltrated, calcareous water is dripping daily from the ceiling into the cavern, in which the CO₂ partial pressure is the same as in the atmosphere. Stalactites are forming (Fig. 41) – why and in which amount per year?

How many mm per year do the stalactites grow assuming that the density of calcite is 2.7 g/cm^3 and that approximately 15 % of the cavern ceiling is covered with stalactites?



Fig. 41 Formation of stalactites in karst caverns

3.1.2.5 Evaporation

Evaporation changes the rainwater chemistry in the sense of a relative depletion of volatile components and a relative enrichment of non-volatile components.

As the calculation of the evaporation is quite tricky in PHREEQC, the following example is given for orientation. It is important to know that 1 kg of water consists of approximately 55.5 mol of H_2O . First, a titration with a negative amount of water (in mol) will be done, in order to remove pure water. Afterwards, the resulting, enriched solution has to be reconverted to 55.5mol by mixing the solution with itself.

Title 90 % evaporation as example

Solution 1 rainwater

.....

REACTION 1

evaporation

H2O -1.0

remove water by $-\text{H}_2\text{O}$!


```

49.95 moles      #90 % evaporation; 100% = 1 kg H2O = 55.5 mol =>
                  #90% = 49.95 mol
                  #the resulting 10 % of the original amount of water
                  #have the same chemical composition as the 100 %
                  #before => the same amount of substance in less
                  #solvent, i.e. an enrichment has taken place

save solution 2
END
MIX
2      10      # mix SOLUTION 2 10 times with itself
                  # to get back to 100 % of enriched solution

save solution 3
END
....further reactions, e.g. equilibrium reactions etc.

```

Calculate the composition of seepage water with and without considering evaporation assuming that the annual average precipitation in an area is 250 mm, the current evaporation is 225 mm and the surface runoff is 20 mm. Use the rainwater analysis of exercise chapter 3.1.2.1. Furthermore, there is an increased CO₂ partial pressure of 0.01 bar in the unsaturated zone. This unsaturated zone consists mainly of limestone and sandstone.

Calculate the amount of calcite being dissolved every year in an area of 50 km · 30 km. How large is the volume of cavities created by this kind of karst weathering assuming a density of calcite of 2.6 g/cm³? How much is the theoretical subsidence resulting from the calcite dissolution per year over the whole area of 50 km · 30 km? (Formation of caverns first prevents an immediate subsidence. Only after those caverns collapse, site specific subsidence structures appear at the surface. This aspect of time and spatial distribution shall be neglected for the calculations above.)

3.1.3 Groundwater

3.1.3.1 The pE-pH diagram for the system iron

In chapter 1.1.5.2.3, using the example of the system Fe-O₂-H₂O, it was demonstrated that the distributions of species can be determined analytically under different pH- and redox conditions and illustrated in a pE-pH-diagram. In the following examples, the numerical solution will be modeled with the help of PHREEQC.

The modeling is relatively simple. In the input file, certain pE- and pH values have to be defined besides the species in solution. After the modeling, the dominant species (i.e. the species with the highest concentration) has to be determined from the species distribution in the output. Varying the pH value between e.g. 0 (acid) and 14 (alkaline) as well as the pE value between e.g. -10 (reducing) and +20 (oxidizing) and listing the dominant species for each pE-pH

combination creates a pE-pH-diagram as a raster image. The smaller the increment (=step width) for the variation of pE and pH is chosen, the finer the raster of the pE-pH-diagram will be.

To avoid entering every pE and pH combination individually (e.g.: using an increment of 1 for pH and pE there would be 15 pH values x 31 pE values = 465 combinations!), a BASIC program was written. It copies a PHREEQC master input file, in which the job is defined for any pE and pH value once, and changes pE and pH step by step. The program can be found on the CD enclosed in this book ("ph_pe_diagramm.exe"). The program is asking for pH- and pE minimum values, maximum values and the increment ("delta"). Furthermore, the existing PHREEQC master input file and a new output file have to be chosen.

The program takes into account that aquatic species are limited in every pE-pH-diagram by the stability field of water. Therefore, the program deletes automatically all pE-pH combinations lying above the line of transformation O_2-H_2O or below the line of transformation H_2O-H_2 . Assistance to the program can be found within the menu HELP.

When considering the increment of 1 for pE and pH, i.e. 15 pH values · 31 pE values, the output file would comprise 465 jobs, numbered from SOLUTION 1 to SOLUTION 465, each containing different pE- and pH values. In fact, there will be only 377 jobs since the SOLUTIONs with pE-pH values above or below the stability field of water are missing. The water constituents defined under SOLUTION (e.g. Fe, Ca, Cl, C, S, etc.) are alike in all 377 jobs. Opening this input file takes about 30 seconds. Because files larger than 32 k cannot be opened in the Windows environment of PHREEQC either they have to be divided into smaller files or they have to be started directly with phreeqc.exe in the DOS prompt (phreeqc Input-File-Name Output-File-Name Database name).

To avoid looking for the predominant species in 377 output jobs manually after modeling, two means are offered: At first, a SELECTED_OUTPUT (see also chapter 2.2.1.4) has to be defined in the PHREEQC master input file. Besides pE and pH, it will output all species of interest, for example all Fe species, in a .csv file. These species have to be specified explicitly under the sub key word "-molalities", e.g. Fe²⁺, Fe³⁺, FeOH⁺, etc. The BASIC-reproduction program inserts the 377 SOLUTION jobs before the key word SELECTED_OUTPUT. Since the SOLUTIONs are not separated by an END, a SELECTED_OUTPUT will be created out of all SOLUTIONs displaying for each of the 377 jobs a row with the columns pH, pE, m_Fe²⁺ (concentration of Fe²⁺ in mol/L), m_Fe³⁺, m_FeOH⁺, etc.

To open and to view this csv file use GRID in PHREEQC. The species with the highest concentration (predominant species) have to be determined for each row (i.e. for each pE-pH combination). To avoid doing this manually, the data have to be copied into EXCEL and to be treated with a macro, which can also be found on the CD enclosed in this book. The macro can be activated by opening the Excel file "macro.xls" from the book's CD and by clicking on "activate macros". Now, one can either copy data instead of the given test data into table 1 or open the .csv file directly in Excel. The activated macro is available for all open Excel files. The macro itself can be opened under menu Extras / Macro / Macros under the name

“maxwert”. Using the menu “edit”, the macro can be viewed and edited. Also the data range as well as the number of rows and columns for the data range has to be defined under “edit”. The definition for the test data follows:

Sub maxvalue

‘ adjust N% and M% as well as the data range

N% = **6**; M% = **4** ‘ N% = number of rows, M% = number of columns

Dim name As Range

Dim wert As Range

Set name = Worksheets(**“Table1”**).Range(**“A1:D1”**)

Set wert = Worksheets(**“Table1”**).Range(**“A1:D6”**)

The values marked in bold have to be changed according to the current data range. If data has been pasted into table 1 replacing the test data, the name of the worksheet needs no further modification. If the .csv file has been opened directly, the name of the current worksheet has to be entered in the macro.

The macro is started using the play button (▶) or the menu Execute/Execute SubUserForm. Then the macro automatically scans each row for the cell with the highest value (= the highest concentration). The columns pH and pE are skipped automatically. For each cell found with a maximum value the respective header cell is written into the first empty row right next to the defined data range. The completed EXCEL table finally has one column more than the original .csv file, in which the names of the predominant species for each pE-pH combination are given (Attention: If the data range has been defined too small by mistake, the program will overwrite a column of the original data!). Note: The macro neither closes automatically nor displays the end of the calculation. The calculation will be finished after approximately 5 seconds at the most. After that, the Microsoft Visual BASIC window has to be closed manually to go back to the modified EXCEL table.

With the 3 columns pE, pH and predominant species, a pE-pH-diagram can be generated as a raster image in Excel. The first step is to sort all three columns according to the column “predominant species” (menu Data / Sorting). The most suitable diagram type is scatter plot (XY) with X = pH and Y = pE. When highlighting the columns pE and pH and creating a scatter diagram all points will appear automatically in the same color (Note: To obtain a raster object choose a filled rectangle as point symbol by double-clicking on the XY points. Vary the size of the rectangles so that a completely filled surface results, approximately 20 pt).

If the individual predominant species appear each in a different color, click with the right mouse button in the diagram and choose the window “data source”. Under “row” you can define a data series for each species (per default, there is only one data set with the name “pe” comprising all species). Further data series can be defined by using “Add”, e.g. the series Fe²⁺, with name (Fe²⁺), X value (as found in the table, e.g. in column A from row 146 to 268) and the respective Y values (B 146 – B 268). The X and Y values can be defined most simply by clicking with the mouse on the red arrow beside the cells for X values and Y

values and mark the respective cells in the table (A146-A268 for X, B146-B268 for Y). As soon as a data set has been defined for each species, different colors will be assigned to them automatically. A raster-pe-pH-diagram is obtained reflecting the predominance of individual species by differently colored zones.

Create a pE-pH-diagram of the predominant iron species in a solution, which contains 10 mmol/L Fe and 10 mmol/L Cl. Vary pH and pE values from 0 to 14 and from -10 to +20, respectively, in steps of 1 as well as of 0.5.

Note: When varying pH and pE in steps of 0.5 the generated PHREEQC input file will be too large to open it within the PHREEQC Windows environment. Therefore, either start PHREEQC from the DOS-prompt or divide the input file in 4 files (a = pH 0-7, pE -10 to +5; b = pH 0-7, pE 5.5-20; c = pH 7.5-14, pE -10 to +5; d = pH 7.5-14, pE 5.5-20).

3.1.3.2 The Fe pE-pH diagram considering carbon and sulfur

How does the pE-pH diagram created in chapter 3.1.3.1 change when 10 mmol/L S(6) or 10 mmol/L C (4) in solution are taken into account?

3.1.3.3 The pH dependency of uranium species

An acid mine water mixes downstream of a mine with groundwater of the following chemical composition (Table 33).

Table 33 Water analysis of an acid mine drainage AMD (pH = 2,3) and of a groundwater GW (pH = 6,6) (concentrations in mg/L)

	GW	AMD		GW	AMD		GW	AMD
pE	6.08	10.56	Cu	0.005	3	Ni	0.005	5
Temperature	10	10	F	0.5	1	NO ₃ ⁻	0.5	100
Al	3.0	200	Fe	0.6	600	Pb	0.05	0.2
As	0.004	2	K	1.5	4	pH	6.6	2.3
C(4)	130		Li	0.02	0.1	Si	3.64	50
Ca	36.6	400	Mg	3.5	50	SO ₄ ²⁻	14.3	5000
Cd	0.0003	1	Mn	0.07	20	U	0.005	40
Cl	2.1	450	Na	5.8	500			

How do the uranium species change? Which species predominate at which pH value? What are the effects of the change in uranium species concerning processes of transport and sorption?

Note: The PHREEQC key word for the mixing of two waters is MIX. Here you have to enter the number of the solution and the percentage, to which the solution contributes to the mixture. Assuming a mixture of 25 % from solution 1 and 75 % from solution 2 may be expressed in the one or the other form:

```

MIX           MIX
  1 0.25      1 1
  2 0.75      2 3

```

When mixing the acid mine drainage, assume that it will be diluted 1:1 with groundwater. Dilute this water again 1:1 with groundwater and so on until you obtain more or less pure groundwater. Save the first 1:1 diluted solution using the key word `SAVE_SOLUTION 3`, terminate the job with `END`, and start the next job with `USE_SOLUTION 3`, etc.

3.1.4 Origin of groundwater

Inverse modeling

The determination of the origin of groundwater is an important aspect of hydrogeological investigations. For establishing drinking water protection zones e.g. it is necessary to know the groundwater's origin to determine possible geogenic or anthropogenic contamination potential and its impact on the extracted groundwater.

The basic idea is to reconstruct geochemical evolution of the groundwater from its chemical composition. For example, knowing the chemical composition of a well on the one hand and an analysis of the rainwater on the other, it will be possible to reconstruct which geological formation the rainwater must have passed after its infiltration to change its chemical composition as the result of reactions with mineral and gas phases (dissolution, precipitation, degassing) in a way that accounts for the composition of the water from the well.

The key word in PHREEQC is "Inverse Modeling". The primary solution(s) (rainwater) and the final product (well water) have to be defined as SOLUTION as well as the involved mineral- and gas phases as PHASES. The structure of such a job follows:

```

TITLE Inverse Modeling
SOLUTION 1          # original water (rainwater)
SOLUTION 2          # water after the reaction with minerals and gases
                   # (well water)
INVERSE MODELING
- solutions 1 2     # solution 1 transforms into solution 2
- uncertainty 0.1  # 10 % uncertainty equally defined for all elements in
                   # the analysis and both waters 1 and 2
- balance Ca 0.2 0.3 # for special elements higher uncertainties can
                   # be defined, e.g. for elements whose
                   # determination underlies a greater error,
                   # e.g. 20 % error for the amount of Ca in
                   # solution 1 and 30 % error for the amount of
                   # Ca in solution 2
- phases           # definition of involved phases

```

```

K-mica    dissolve    # mica can only be dissolved
CO2(g)    # both dissolution and degassing possible
SiO2(a)   # both dissolution and precipitation possible
Kaolinite precip    # allow only for precipitation

```

```

END                # end of the job

```

Note: For each element in solution 1 or solution 2, a mineral or gas phase has to be defined under PHASES that contains this element. Otherwise PHREEQC reports the following problem: “element is included in solution 1, but is not included as a mass-balance constraint”. The modeling can still be continued, however the respective element is not considered for the mass balance.

The number of the mineral phases as well as the size of the uncertainty should be varied to simulate different possible situations. Maybe the program does not find a valid model after the first calculation. Then the mineral phases have to be changed or completed or the uncertainty has to be increased, whereas of course uncertainties of > 10 % do not permit any reliable predictions anymore. Also including as many mineral and gas phases as possible, does not help. The main goal is to exclude as many reaction pathways as possible and find others with a minimum of necessary gas and mineral phases.

Depending on the number of mineral phases and the uncertainty chosen the program displays one or more models in the output. Each model describes how much of each mineral was dissolved or precipitated to transform solution 1 (rainwater) into solution 2 (well water) (key word: phase mole transfers). If you enter several initial solutions (e.g. 5 analyses of rainwater from 5 individual altitudes), the program will also calculate the share of the respective rainwater solutions contributing to the final solution (well water).

3.1.4.1 Origin of spring water

Inverse modeling is to be carried out for the spring water in the eastern part of the model area (Fig. 40) to determine the geological formation from which the spring water originates. The hydrogeochemical data can be found in Table 34.

Table 34 Water analysis of a spring water (concentrations in mg/L)

pH	6.5		
Redox potential	-120 mV	Al	0.26
Temperature	10.7 °C	SiO ₂	24.68
O ₂	0.49	Cl	12.76
Ca	64.13	HCO ₃	259.93
Mg	12.16	SO ₄	16.67
Na	20.55	H ₂ S	2.33
K	2.69	NO ₃	14.67
Fe	0.248	NH ₄	0.35
Mn	0.06	NO ₂	0.001

Analysis of the rainwater:

Na=323, K=65, Ca=165, Mg=120, SO_4^{2-} =712, NO_3^- =205, HCO_3^- =527, Cl=234 [concentrations in $\mu\text{g/L}$]; pH: 5.1, temperature: 21°C.

Mineralogical investigations showed that the following trace minerals exist additionally to the main minerals in the following geological formations:

- $\text{Fe}(\text{OH})_{2.7}\text{Cl}_{0.3}$, FeS_2 , MnO_2 , arsenolite in the crystalline basement
- NaCl and $\text{CaMg}(\text{CO}_3)_2$ in the Cretaceous limestones
- FeOOH , Ca-montmorillonite and K-mica in the Quaternary sediments

Proceed with the assumption that neither feldspars nor mica nor halite nor gypsum will form under the given conditions. However, clay minerals such as Ca montmorillonite can precipitate.

Give reasons for your chosen model regarding the special geological location of the spring and try to use a minimum of mineral phases.

[see exercise chapter 3.1.1.9 for definition of a data set of non-existent species]

3.1.4.2 Pumping of fossil groundwater in arid regions

50 L/s groundwater of the following composition (Table 35) are extracted from a well in an arid zone.

Table 35 Water analysis of a groundwater (pH = 6.70, temperature = 34.5 °C, concentrations in mg/L)

K	2.42	Na	12.96	Ca	247.77	Mg	46.46
Alkalinity	253.77	Cl	6.56	NO_3^-	2.44	SO_4^{2-}	637.75
SiO_2	4.58	^{13}C	-6 ± 0.8	^2H	-68 ± 0.6	^{18}O	-9.6 ± 0.3

It is known that only a small amount of the extracted groundwater originates from recent groundwater resources (Table 36). The rest is extracted from a reservoir of fossil water that has been formed 20.000 years ago when temperatures were considerably lower in that area than they are today.

The fossil water is characterised by high total mineralization as a result of long residence times in the subsurface as well as by lower ^2H and ^{18}O isotope values as a result of the lower temperatures during formation (Table 37). The different amounts of ^{13}C can be explained by the establishment of equilibrium of the fossil groundwater with marine limestones with higher amounts of ^{13}C than recent groundwater, which reflects the lower concentrations of ^{13}C in the atmosphere.

Table 36 Water analysis of a recent groundwater (pH = 6.70, temperature = 28.0 °C, concentrations in mg/L)

K	2.87	Na	14.60	Ca	72.60	Mg	20.50
Alkalinity	247.97	Cl	4.00	NO_3^-	4.52	SO_4^{2-}	69.96
SiO_2	32.16	^{13}C	-22 ± 1.4	^2H	-52 ± 0.5	^{18}O	-7.5 ± 0.3

Table 37 Water analysis of a fossil groundwater (pH = 6.90, temperature = 40 °C, concentrations in mg/L)

K	3.33	Na	18.41	Ca	351.80	Mg	65.96
Alkalinity	298.29	Cl	9.00	NO ₃ ⁻	1.35	SO ₄ ²⁻	906.15
SiO ₂	20.74	¹³ C	0 ± 0.4	² H	-76 ± 0.7	¹⁸ O	-10.5 ± 0.4

Apply inverse modeling to determine how much of the extracted groundwater originates from the reservoir of fossil water. Also take into account that the extracted groundwater has been in contact with sandstones, dolomitic limestones, gypsum and halite and that under the given conditions neither dolomite nor gypsum nor halite are formed. Assume precipitation for calcite and degassing of CO₂.

If the amount of fossil water in the extracted groundwater is known an estimation can be given on how long it will take to completely exploit the approximately 5 m high, 1 km wide and 10 km long reservoir assuming a constant rate of production of 5 L/s.

Note: Remember the explanation in the introduction of chapter 3.1.4 that the portions of several initial solutions on the final solution can be modeled with the help of the inverse modeling!

To include the isotopes in the modeling, they have to be defined under each respective SOLUTION using the sub keyword "isotope".

SOLUTION

-isotope [name of the isotope in the following form: mass number element] [value in %, pmc or as ratio] [uncertainty in % (possible, but not necessary)], e.g.

-isotope 13C -6 0.8

Instead of the sub key words -isotope the abbreviation -i can be used.

Isotope data can only be used for inverse modeling. There, the respective isotopes have to be listed again under the key word Inverse_Modeling and under the sub key word -isotopes, e.g.

INVERSE_MODELING

-isotopes

13C

2H

18O

Additionally for each mineral or gas phase containing these isotopes their share has to be defined (mean value, in the example 2 ‰ and deviation, in the example ± 2 ‰) and whether the respective phase shall be dissolved or precipitated, e.g.

-phases

calcite pre 13C 2.0 2

Consider an average concentration of 13C between 1-5 ‰ for dolomite, 0-4 ‰ for calcite and -20 to -30 ‰ for CO₂. The isotopes ²H and ¹⁸O can only be found in the water molecule. Therefore they do not have to be defined for a mineral phase.

If you want to keep the option of dissolution or precipitation open, define the mineral phases twice, once using dis (dissolve), and a second time using pre (precipitate).

3.1.4.3 Salt water / fresh water interface

As a result of the groundwater extraction in coastal areas, seawater intrusions occur, leading to a mixture of salt water and fresh water. Such a mixed ground water of the following chemical composition is extracted from the irrigation water well B1 in the model area west of the town (Fig. 40): pH = 6.58, temperature = 13.4 °C, Ca = 3.724e-03 mol/L, Mg = 1.362e-02 mol/L, Na = 1.080e-01 mol/L, K = 2.500e-03 mol/L, C = 7.067e-03 mol/L, S = 6.780e-03 mol/L, Cl = 1.261e-01 mol/L, P = 7.542e-06 mol/L, Mn = 8.384e-10 mol/L, Si = 1.641e-05 mol/L, Fe = 8.248e-09 mol/L.

The results of the analysis of the seawater are as follows: pH = 8.22, temperature = 5.0 °C, Ca = 412.3 mg/L, Mg = 1291.8 mg/L, Na = 10768.0 mg/L, K = 399.1 mg/L, HCO₃⁻ = 141.682 mg/L, SO₄²⁻ = 2712.0 mg/L, Cl = 19353.0 mg/L, Si = 4.28 mg/L, Mn = 0.0002 mg/L, Fe = 0.002 mg/L. Furthermore, consider a higher density for seawater (1.023 g/cm³)!

The following analysis is given for the Quaternary aquifer: pH = 6.9, temperature = 18 °C, Ca = 65.9 mg/L, Mg = 40.1 mg/L, Na = 3.5 mg/L, K = 7.5 mg/L, HCO₃⁻ = 405.09 mg/L, SO₄²⁻ = 23.4 mg/L, Cl = 15.8 mg/L, PO₄³⁻ = 0.921 mg/L.

Determine the origin of the mixed ground water (i.e. the share of seawater and fresh ground water) taking into account the geological features around the irrigation water well. Keep in mind that there is no distinct aquiclude between the Quaternary and the Cretaceous aquifer.

Note: In general, check each analysis regarding the analytical error and enforce, if necessary, a charge balance when the deviations are too high before starting the modeling.

3.1.5 Anthropogenic use of groundwater

3.1.5.1 Sampling: Ca titration with EDTA

To determine the amount of calcium in a water sample, e.g. the titration with EDTA (ethylenediaminetetraacetate, C₂H₄N₂(CH₂COOH)₄) can be used. First of all, NaOH is added to the sample to obtain a pH value of at least 12. Then, a color indicator is admixed and titration with EDTA performed until the color changes. In doing so, all Ca is converted to a Ca-EDTA complex and detected in this form.

Model the determination of the concentration of Ca of the following analysis with PHREEQC: pH = 6.7, temperature = 10.5 °C, Ca²⁺ = 185 mg/L, Mg²⁺ = 21 mg/L, Na⁺ = 8 mg/L, K⁺ = 5 mg/L, C(4) = 4.5 mmol/L, SO₄²⁻ = 200 mg/L, Cl = 90 mg/L, NO₃⁻ = 100 mg/L.

The amount of EDTA that has to be added until the color changes is unknown. Therefore, EDTA is added step by step and the titration is continued beyond the point of color change. The point of color change will be determined afterwards using the obtained graph.

[EDTA cannot be found in the previously used data set WATEQ4F.dat. It is only defined in the data set MINTEQ.dat. Therefore, use this one. The key word for the addition of EDTA is the same as for the exercise in chapter 3.1.1.9.]

3.1.5.2 Carbonic acid aggressiveness

In drinking water standards it is often required that “water should not be aggressive”. In most cases this “aggressiveness” refers to the carbonic acid. The reason for the requirement of a low aggressiveness is not of toxicological but of technical nature since carbonic acid waters easily corrode materials of pipelines (concrete, metals, plastics). Regulations therefore recommend, that the measured pH value shall only differ ± 0.2 pH units from the pHc (the pH value at calcite saturation) ($\Delta\text{pH} = \text{pH} - \text{pHc}$). The aim is to have a pH value that is slightly above the pHc value (0.05 pH units) because then a protective layer can develop on the pipe walls. On the contrary, significant supersaturation ($\Delta\text{pH} > 0.2$) lead to noticeable calcite deposits within the pipes and calcite scales are as undesirable as undersaturation ($\Delta\text{pH} < -0.2$), which leads to corrosion.

Additionally, potable water should not exceed pH values of 9.5 or fall below pH values of 6.5.

Consider these technical requirements when checking if the potable water extracted from the drinking water well B3 in the model area (chapter 3.1.1.1, Fig. 40) can be used without further treatment.

3.1.5.3 Water treatment by aeration - well water

Check whether an open aeration from equilibrium with atmospheric CO_2 (open system) would help to meet the requirements concerning the pH as well as the ΔpH for the drinking water which is extracted from well B3 in the model area (Fig. 40).

[Note: For simulating the open aeration and the calculation of the new pHc in one job, use the commands SAVE_SOLUTION, END and USE_SOLUTION 1 like in the exercise in chapter 3.1.3.3.]

3.1.5.4 Water treatment by aeration - sulfur spring

For the little village as well as for some individual farms in the eastern part of the model area (Fig. 40), a possibility for drinking water supply is sought. The spring discharging east of the village shall be investigated for suitability. Its chemical composition is given in chapter 3.1.4.1, where its geological origin has already been modeled.

Illustrate the species distribution for the elements aluminium, iron(II) and iron(III). Then, model a water treatment in terms of an open aeration with atmospheric oxygen (oxidation!). What happens to the Al- and Fe species? Which mineral phases will presumably precipitate during the aeration?

Vary the partial pressure of oxygen. What is remarkable?

Is the pH value after the aeration still within the limits required for potable water?

To set up the dimensions of a water treatment plant correctly, it is important to know the amount of sludge that will form every day as the result of the precipitation of mineral phases. Enforce the precipitation of the mineral phases that are most likely to precipitate during aeration in your model and calculate the accumulating amount of sludge per day assuming a production rate of 30 L/s in the future water treatment plant. Do not forget that sludge does not only consist of the precipitated mineral phases but mainly of water (60-90 %).

Evaluate your model with regard to the elements N and S. What will the results rather look like in reality and why?

3.1.5.5 Mixing of waters

Not far from the drinking water well B3 in the model area (Fig. 40) there is an older, abandoned well B4 that has been shut down for several years as it did not meet the quality requirements for potable water anymore. Recent investigations showed the following result: pH = 6.99, temperature = 26.9°C, $\text{Ca}^{2+} = 260 \text{ mg/L}$, $\text{Mg}^{2+} = 18 \text{ mg/L}$, $\text{Na}^+ = 5 \text{ mg/L}$, $\text{K}^+ = 2 \text{ mg/L}$, $\text{HCO}_3^- = 4 \text{ mmol/L}$, $\text{SO}_4^{2-} = 260 \text{ mg/L}$, $\text{Cl}^- = 130 \text{ mg/L}$, $\text{NO}_3^- = 70 \text{ mg/L}$.

It is planned to reactivate the well B4 to support peak times of water consumption and to mix the extracted water with that of the current drinking water well B3. Check with the help of PHREEQC modeling if and in which shares this can be done with regard to general requirements of drinking water standards and to the technical requirements in terms of the calcite-carbondioxide equilibrium (chapter 3.1.5.2). [*key word for mixing of two waters see the exercise in chapter 3.1.3.3.*]

3.1.6 Rehabilitation of groundwater

3.1.6.1 Reduction of nitrate with methanol

Groundwater from the exercise in chapter 3.1.5.1 in an area with intensive agriculture shows extremely high concentrations of nitrate due to years of excessive fertilization. Methanol as a reducing agent shall be pumped into the aquifer via infiltration wells to reduce the pentavalent nitrogen (nitrate) to the zero valent gas nitrogen. The latter can degas leading to a decrease of nitrate concentrations in the aquifer. How many liters of a 100 % methanol solution (density of methanol = 0.7 g/cm^3) per m^3 aquifer have to be pumped into the

aquifer to guarantee an effective reduction of nitrate concentrations? What effect could an “overdose” of methanol have?

3.1.6.2 *Fe(0) barriers*

Reactive barriers of elemental iron are used to reduce groundwater constituents in-situ and thus, to convert e.g. mobile uranium(VI) into uranium(IV) that precipitates as uraninite (UO_2). At the same time, the elemental iron in the reactive barriers oxidizes and iron hydroxide and, secondary, crusts of iron oxide form. Precipitated iron hydroxides and uraninite reduce the reactivity of the barrier after a certain time.

The uranium containing mine water of the exercise in chapter 3.1.3.3 shall be cleaned by means of such a reactive barrier. How much iron per m^2 has to be used considering a percolation of the reactive barrier of $500 \text{ L/d}\cdot\text{m}^2$ to reduce the amount of uranium from 40 mg/L to at least one third taking into account that the barrier shall be in operation for approximately 15 years? How much uraninite will precipitate?

3.1.6.3 *Increase in pH through a calcite barrier*

To increase the pH of the acid mine drainage from the exercise in chapter 3.1.6.2 a reactive wall of 1 m thick calcite (density of calcite = 2500 kg/m^3) shall be installed within the aquifer. Thickness and permeability of the wall are chosen in a way that a 50 % saturation of lime in the aquifer can be reached with a daily percolation of 500 L/m^2 .

Does the calcite wall lead to the desired increase of the pH value? And why are there still objections against the reactive calcite wall taking into account the long-term efficiency and premature alteration? Which carbonates could be chosen alternatively to calcium carbonate to avoid a premature alteration?

3.2 Reaction kinetics

3.2.1 *Pyrite weathering*

Diffusion calculations for a covered heap containing pyrite rocks show that 0.1 m^3 of oxygen enter the heap every day by diffusion. It is assumed that this oxygen is completely consumed by pyrite oxidation within one day. Therefore, reaction kinetics is exclusively determined by the diffusion rate of the oxygen into the heap. An average of 0.1 mm of rainwater infiltrates through the heap cover daily. The rainwater has a pH of 5.3, a temperature of $12 \text{ }^\circ\text{C}$ and is in equilibrium with the CO_2 and O_2 partial pressure of the atmosphere. The heap covers an area of $100 \text{ m} \times 100 \text{ m}$, has a height of 10 m, and a pyrite concentration of 2 Vol%. The following questions are to be solved:

1. What is the chemical composition of the seepage water discharging at the foot of the heap along the base sealing?
2. What happens when water at the foot of the heap gets in contact with atmospheric oxygen?
3. How many years will it take until all pyrite in the heap is exhausted?
4. How much carbonate has to be added during the heap construction to neutralise the pH value? Is it possible to reduce the amount of sulfate at the same time?
5. How does the necessary amount of carbonate change when assuming that a CO₂ partial pressure of 10 Vol% will develop within the heap as a result of the decomposition of organic matter?

Instead of assuming an oxygen diffusion rate as in this example, it is also possible to define a pyrite oxidation rate R that is a function of e.g. O₂, pH, temperature, the amount of microorganisms and the nutrient supply. Examples using direct reaction rates in PHREEQC follow in the next exercises.

3.2.2 Quartz-feldspar-dissolution

Model the dissolution of quartz and K-feldspar (adularia) over time. Are the parameters temperature and CO₂ partial pressure of any importance? Within the key word RATES use the BASIC program from the data set PHREEQC.dat. The calculation is done with distilled water (pH = 7, pE = 12) as a batch reaction over a time span of 10 years in 100 time steps at a temperatures of 5 °C and of 25 °C and at CO₂ partial pressures of 0.035 Vol% (atmosphere) and of 0.7 Vol% (soil). Calculate also the kinetics of the dissolution with 0.035 Vol% CO₂ and 25 °C for a period of 10 minutes.

[Note: The data set WATEQ4F.dat uses the name adularia for K-feldspar. Use EQUILIBRIUM_PHASES to fix the oxygen concentration to 21 Vol%. Enter quartz with "0 0" under the same key word. While the first zero limits the solubility to 100% saturation, the second zero indicates the possible amount of quartz added in moles. Zero means no further quartz addition (dissolution), i.e. that the 100% saturation can only be achieved through precipitation at supersaturation, but not through dissolution at undersaturation. This step is necessary, since the dissolution will be defined using KINETICS and RATES. It is quite useful, too, to limit the solubility of aluminium by the precipitation of e.g. kaolinite. In the simplest case this can be done by EQUILIBRIUM_PHASES as well since this precipitation occurs spontaneous and fast. Thus, a kinetic modeling is not necessary.]

Using the minerals quartz and kaolinite in EQUILIBRIUM_PHASES causes a problem in PHREEQC regarding the elements Si and Al because they do not occur within the key word SOLUTION. Therefore you have to specify them in very small quantities in the solution (e.g. 1 µg/L). Furthermore, the sub key word -step_divide 100 within the key word KINETICS is necessary. The output can be obtained most effectively using SELECTED_OUTPUT.]

3.2.3 Degradation of organic matter within the aquifer on reduction of redox sensitive elements (Fe, As, U, Cu, Mn, S)

The degradation of organic matter results in the consumption of oxygen. Under certain circumstances, this may lead to the reduction of oxygen-containing anions like nitrate (see also the exercise in chapter 3.1.6.1) and sulfate, as well as to the reduction of redox sensitive elements like iron, manganese, or uranium. The decomposition of organic matter depends on the presence of microorganisms and is thus always connected to kinetics.

The reactions in an aquifer shall be modeled in the presence of calcite and large concentrations of pyrite and organic matter for the acid mine drainage from the exercise in chapter 3.1.3.3. As no inorganic carbon is given in the analysis and calcite is to be used as kinetically reacting mineral in the model, the analysis has to be completed by e.g. 1 mg/L carbon, formally.

PHREEQC always refers to one liter or one kg of water. The model describes a batch reaction with 1 liter water. 10 mmol calcite as well as 1 mol pyrite and 1 mol organic matter shall be present in the respective sediment/rock. To describe the kinetics of calcite and pyrite, the BASIC program given at the end of the data set PHREEQC.dat is used. For the degradation of organic matter the PHREEQC.dat notation is used, too. However, the lines 50 and 60 have to be changed as follows to accelerate the decomposition of the organic matter. Nitrate is not taken into account in this example.

```
50 rate = 1.57e-7*mO2/(2.94e-4 + mO2)
```

```
60 rate = rate + 1.e-10*mSO4/(1.e-4 + mSO4)
```

Since there is no general definition for organic matter in any of the three data sets which are installed with the PHREEQC program, a name has to be assigned in the kinetics data block (e.g. Organic_C) and the organic matter has to be specified using the key word “-formula”. Use the general formula CH_2O .

```
-formula CH2O
```

KINETICS needs three subdivisions for organic matter, pyrite and calcite, respectively. It is not relevant, in which block the time steps are defined. Using “-step_divide 1000000”, the step width is cut down at the beginning of the kinetic calculations according to the quotient total time/step_divide.

Since all calcite is dissolved after 100 days at the latest, the following line for the calcite kinetics is inserted at the beginning of the BASIC program to save calculation time:

```
5 if time > 8640000 then goto 200
```

The simulation time is 10.000 days in 100 intervals (steps). For a higher temporal resolution at the beginning of the simulation, another model with only 600 days in 100 intervals will be calculated afterwards.

3.2.4 Degradation of tritium in the unsaturated zone

If the unsaturated zone is composed of relatively fine sediment (silt and fine sands) a quasi-uniform seepage flow can be assumed for the unsaturated zone in humid climate zones over long time spans. Therefore, the transport of infiltration water can be simulated in PHREEQC as a monotonous movement in accordance with the "piston flow" model. A constant flow of infiltration water of 0.5 m per year is assumed for the following simulation. Furthermore, it is considered simplistically that the infiltrating precipitation has a tritium activity of 2000 TU (tritium units) over a period of 10 years. Then, it is assumed that the tritium activity decreases to zero again.

The following example shows how this can be modeled in PHREEQC. First of all, a master- and a solution species tritium T or T⁺ have to be defined. Since the input of data for log_k und -gamma within the key word SOLUTION_SPECIES is required, but unknown, any value can be entered here as a free parameter ("dummy", e.g. 0.0). This value is not used for kinetic calculations and thus, does not cause any problems. However, all results based on equilibrium calculations (e.g. the calculation of the saturation index) are nonsense for this "species". The tritium values have to be entered in tritium units. However, in order not to have to define or convert them in an extra step, they are entered fictitiously with the unit umol/kgw instead of TU in PHREEQC. As no interactions of tritium with any other species are defined, the unit is eventually irrelevant. After modeling, remember that the result is displayed in mol/kgw as always in PHREEQC and has to be recalculated to the fictitious tritium unit umol/kgw. Entering mol/kgw in the input file, the solution algorithm quits due to problems with too high total ionic strengths.

The unsaturated zone is 20 m and is subdivided into 40 cells, 0.5 m each so that a "time step" is exactly 1 year = 86400 * 365 seconds = 3.1536e+7 seconds. The half-life of tritium (12.3 years) has to be entered in seconds in PHREEQC. First, the created 1d soil column is saturated with water containing no tritium (solution 1-40). Then, water with 2000 TU is added over a period of 10 "shifts" (= 10 years) (*Note: solution 0 is always the solution which is added on top of the column*). After this high tritium impulse, the solution is changed again to water containing no tritium, which percolates through the column for another 30 years. The two changes from water with 0 TU to 2000 TU and back again from 2000 TU to 0 TU are two different jobs that have to be separated by END.

The degradation of tritium is described as a 1st order kinetic reaction as follows (see also Table 14):

$$\frac{d(A)}{dt} = -K_k \cdot (A)$$

$$t_{1/2} = \frac{1}{K_k} \cdot \ln 2$$

```

PHREEQC Job: Tritium in the unsaturated zone – impulse like input function
TITLE                                tritium in the unsaturated zone
PRINT
  -reset false                        # no standard output
SOLUTION_MASTER_SPECIES # define master species tritium
T      T+      -1.0      T      1.008
SOLUTION_SPECIES        # define solution species tritium
T+ = T+
  log_k    0.0                # dummy
  -gamma  0.0      0.0        # dummy
  SOLUTION 0 tritium 1.phase    # tritium concentration 2000 TU after
                                # the initial column water with 0 TU
  units    umol/kgw
  temp     25.0
  pH       7.0
  T        2000                # unit umol/kgw, only fictitious
SOLUTION 1-40                # initial column water without tritium
  units    umol/kgw
  temp     25.0
  pH       7.0
END                            # end of the 1st job
RATES                          # define degradation
T                               # for tritium
-start
  10 rate = MOL("T+") * -(0.63/parm(1)) # 1st order kinetics (Table 14)
  20 moles = rate * time
  30 save moles
-end                             # end of the 2nd job
KINETICS 1-40
T
  -parms  3.8745e+8            # 12.3 years in seconds (half-life of
                                tritium)
TRANSPORT
  -cells   40                  # 40 cells
  -length  0.5                 # 0.5 m each, 40 * 0.5 = 20 m length)
  -shifts  10                  # 10 years
  -time_step 3.1536e+7         # 1 year in seconds
  -flow_direction forward      # forward simulation
  -boundary_cond flux flux     # flow boundary condition at inlet
                                # and outlet
  -diffc   0.0e-9              # diffusion coefficient
  -dispersivity 0.05           # dispersivity
  -correct_disp true           # correction of dispersivity yes
  -punch_cells 1-40            # cell 1 to 40 in Selected_output
  -punch_frequency 10          # print every 10th time interval

```


SELECTED_OUTPUT

```

-file    tritium.csv          # output to this file
-reset   false                # no standard output
-totals  T                    # print total tritium concentration
-distance true

END                                             # end of 3rd job
SOLUTION 0                                    # no more tritium after 10 years of
units    umol/kgw             # infiltrating water with 2000 TU
temp     25.0
pH       7.0
TRANSPORT
Shifts   30                    # for another 30 years
END
    
```

Fig. 42 shows a vertical cross section of tritium concentrations resulting from an impulse-like input of tritium into the unsaturated zone after 10, 20, 30 and 40 years. The tritium peak moves downward and widens continuously.

The actual task now is to change the PHREEQC job in such a way that the tritium input function is not impulse-like but more realistic. Fig. 43 illustrates the increase of tritium concentrations in precipitation water from 1962 to 1963 and the subsequent decrease from 1963 to 1997, as determined at the climate station Hof-Hohensaas, Germany.

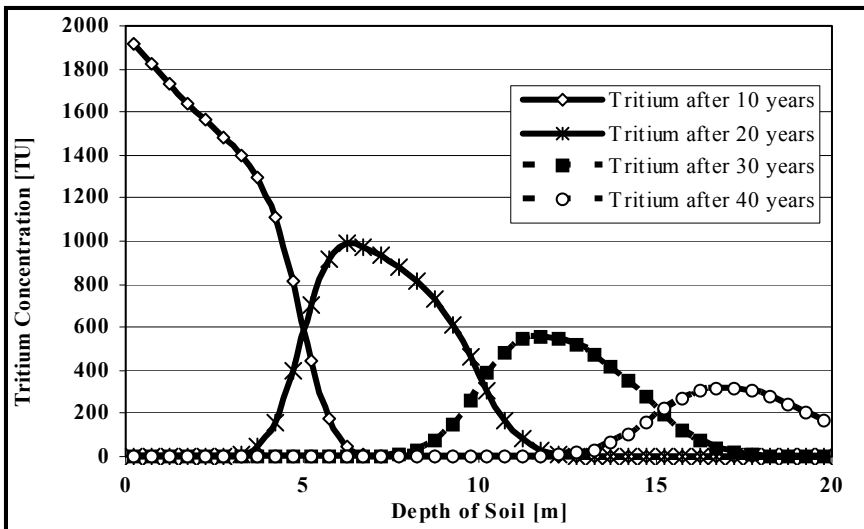


Fig. 42 Vertical cross section of tritium in the unsaturated zone (0-20 m depth) for the time intervals 10, 20, 30, 40 years assuming an impulse-like input during the first ten years

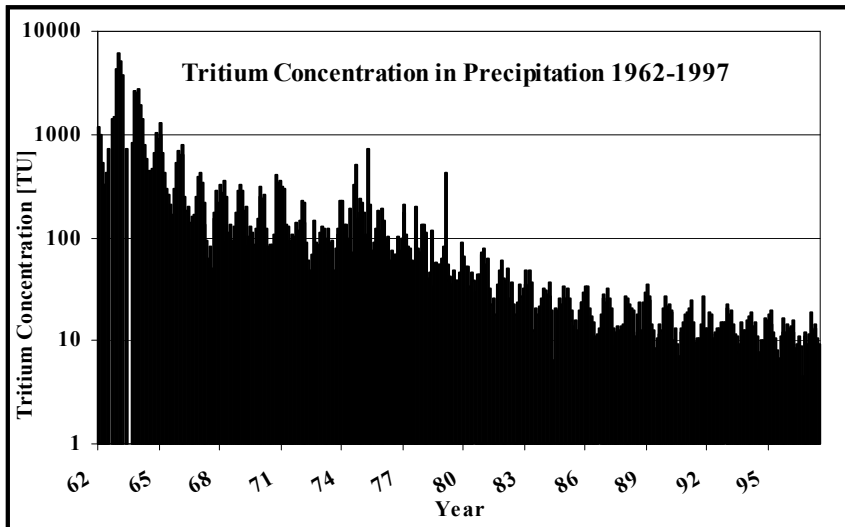


Fig. 43 Tritium concentration in rainwater, measured at the station Hof-Hohensaas, Germany (latitude 50.32 °N, longitude 11.88 °E, height 567 m NN) from 1962 to 1997

The definition of a more realistic tritium input function based on the available data of the tritium concentrations in the rainwater is done in time intervals of 5 years each (Table 38).

Table 38 Tritium concentrations in the atmosphere from 1962 to 1997

Intervall of 5 years	Tritium in the atmosphere (TU)
1 (06/1962 - 06/1967)	1022
2 (07/1967 - 07/1972)	181
3 (08/1972 - 08/1977)	137
4 (09/1977 - 09/1982)	64
5 (10/1982 - 10/1987)	24
6 (11/1987 - 11/1992)	17
7 (12/1992 - 12/1997)	13

Remodel the degradation of tritium in the unsaturated zone with this new input function. Compare your results with the results obtained from the assumption of an impulse-like tritium input in Fig. 42.

3.3 Reactive transport

3.3.1 Lysimeter

A lysimeter filled with sediments was equilibrated with the following water (concentrations in mmol/L):

pH = 8.0, pE = 12, temperature = 10.0 °C, Ca = 1, C = 2.2, Mg = 0.5, K = 0.2, SO_4^{2-} = 0.5

At a time T1, an acid mine drainage of the following composition is added (concentration in mmol/L):

pH = 3.2, pE = 16, temperature = 10.0° C, Ca = 1, C = 2.0, Mg = 0.5, K = 0.2, SO_4^{2-} = 4.0, Fe = 1, Cd = 0.7, Cl = 0.2

Calculate the distribution of the concentrations within the lysimeter column taking into account the cation exchange (discretisation and time steps as in the example in chapter 2.2.2.3). Selectivity coefficients are taken from the exemplary data of WATEQ4F.dat data set and an exchange capacity of 0.0011 mol per kg water is assumed. Neither diffusion nor dispersion is considered. Present your results graphically.

3.3.2 Karst spring discharge

A karst water has the following chemical composition:

pH = 7.6, pE = 14.4, temperature = 8.5 °C, Ca = 147, HCO_3^- = 405, Mg = 22, Na = 5, K = 3, SO_4^{2-} = 25, Cl = 12, NO_3^- = 34

It is in equilibrium with a CO_2 partial pressure of 0.74 Vol% and is slightly supersaturated with regard to calcite (SI = 0.45). This karst water discharges at a spring with a mean discharge of 0.5 L/s and flows in a small channel downhill with a mean velocity of 0.25 m/s. Due to the turbulent flow, CO_2 will degas spontaneously until equilibrium is reached with the CO_2 partial pressure of the atmosphere. Because of the resulting carbonate precipitation, the creek forms a small carbonate ridge over the years, on top of which it flows in a small channel (Fig. 44).

Model the carbonate precipitation in this carbonate channel by means of a 1d transport with 40 cells of 10 m length each. Dispersivity is assumed with 1m. Use the key words KINETICS and RATES and the BASIC program for calcite from the data set PHREEQC.dat describing the kinetics for both the calcite dissolution and the calcite precipitation. How much calcite precipitates each year within the channel's first 400 meter after the discharge? How much CO_2 degasses at the same time?

[Note: For all n cells a SOLUTION has to be defined at the beginning of the modeling (SOLUTION 1- n). The same applies for the key words KINETICS and EQUILIBRIUM PHASES. If you use 1 instead of 1- n , the kinetic or the equilibrium reactions would only be modeled for the first cell.]



Fig. 44 Calcite ridge at a karst spring discharge near Weißenburg, Germany.

3.3.3 Karstification (corrosion along a karst fracture)

Talking about karstification often the question arises why karst phenomena do not only occur at the surface but in greater depths as well. The reason is that the carbonate dissolution is a comparatively fast process, but still takes some time, while water may cover quite a long distance along a fracture.

This shall be modeled with the following example. A fracture with an extension of 300 meters is given. Assume that, at the beginning of the simulation, this fracture is filled with groundwater that is in carbonate equilibrium. To simplify matters the following data shall be used:

pH	7.32
Temp	8.5
C	4.905 mmol/L
Ca	2.174 mmol/L

Infiltrating rainwater now dissolves CO_2 according to the increased partial pressure of 1 Vol% in the unsaturated zone. Thus, the seepage water has the following characteristics:

pH	4.76
Temp	8.5
C	0.5774 mmol/L

This water enters the model fracture with a velocity of 10 m per 6 minutes. Calculate the carbonate dissolution in the 300 meter long fracture, that will be

modeled as a one dimensional pipe with 30 elements of 10 m length each. Furthermore, consider a dispersivity of 0.5 m and assume that the whole water column will be exchanged once. Moreover, the fracture is not completely filled with water, but contains air, too. This air has a CO₂ partial pressure of 1 Vol%. The kinetics of the carbonate dissolution shall be assumed according to chapter 2.2.2.2.1. Further, use the key word USER_GRAPH to visualize the result graphically within PHREEQC. The concentrations of Ca and C as well as the calcite saturation index shall be displayed along the 300 m long fracture after a single exchange with the infiltrating rainwater.

3.3.4 The pH increase of an acid mine water

Acid mine drainages (AMD) cause great problems in the mining industry as they typically contain high concentrations of iron, sulfate and protons due to the pyrite oxidation. Consequently, other elements (e.g. metals and arsenic) may be increased as well. A simple method of water treatment is to conduct these acid waters through a carbonate channel. This process causes an increase of the pH value due to carbonate dissolution. Furthermore it can result in supersaturation of other minerals that can precipitate spontaneously. The high sulfate concentrations combined with increasing calcium values from the calcite dissolution often exceed the gypsum solubility product. Iron minerals are also supersaturated as a result of these reactions, and consequently e.g. amorphous iron hydroxide precipitates spontaneously. Even though the dissolution of calcite is relatively fast this exercise shows that the reaction kinetics still has to be taken into account to plan the dimensions of such a carbonate channel correctly. An acid mine drainage (“AMD”) and a natural surface water are given (Table 39).

Table 39 Water analysis of an acid mine drainage (“AMD”) and of a natural surface water (“SW”)

Parameter	AMD	SW
pe	6.08	6.0
Temp.[°C]	10	10
pH	1.61	8.0
Al	1.13e-04 mol/L	
As	5.47e-07 mol/L	
TIC*)	3.18e-03 mol/L	
HCO ₃ ⁻		130 mg/L **)
Ca	9.19e-04 mol/L	36.6 mg/L***)
Cd	2.27e-07 mol/L	
Cl	6.07e-05 mol/L	2.1 mg/L
Cu	8.06e-07 mol/L	
F	2.69e-05 mol/L	
Fe	2.73e-02 mol/L	0.06 mg/L

Parameter	AMD	SW
K	3.93e-05 mol/L	1.5 mg/L
Li	2.95e-06 mol/L	
Mg	1.47e-04 mol/L	3.5 mg/L
Mn	1.30e-06 mol/L	
NO ₃ ⁻	2.47e-04 mol/L	0.5 mg/L
Na	2.58e-04 mol/L	5.8 mg/L
Ni	8.72e-07 mol/L	
Pb	2.47e-07 mol/L	
SO ₄ ²⁻	5.41e-02 mol/L	14.3 mg/L
Si	6.20e-05 mol/L	3.64 mg/L
U	2.15e-07 mol/L	
Zn	1.09e-05 mol/L	

*) total inorganic carbon

**) adjust inorganic C to the partial pressure of the atmosphere (CO₂(g) -3.5)

***) set Ca to “charge” in the PHREEQC input file

At the beginning of the modeling the 500 m long carbonate channel is filled with the surface water (“SW”). Then, the acid mine water is added. Calculate how the composition of the mine water changes, how much calcite is dissolved and how much gypsum and iron hydroxide precipitate. Additional problems like coating of the carbonate by gypsum and iron hydroxide crusts as well as the kinetics of the formation of gypsum and iron hydroxide are ignored in this model.

Apply 1 m/s as flow velocity so that the total contact time in the channel is 500 seconds. The modeling should be done as 1d transport model with 10 cells (dispersivity: 0.1 m) and last over 750 seconds. Also take into account the contact with the atmosphere. Therefore, run the model once with a CO₂ partial pressure of 0.03 Vol% and a second time with 1 Vol%, both times assuming an oxygen partial pressure of 21 Vol% O₂. The latter case corresponds rather to a closed carbonate channel.

Illustrate the results of the model by presenting the water characteristics over the whole length of the channel at the end of the modeling (pH value, SI calcite, Ca, Fe, C, SO₄²⁻, CaSO₄⁰). Additionally indicate the amounts of calcite dissolved and of gypsum and iron hydroxide precipitated.

3.3.5 In-situ leaching

Aquifers with double porosity (e.g. sandstones with fractures and pore volume) require special considerations with regard to transport modeling even if no reactive mass transport in its proper sense is taken into account. This problem is demonstrated with the following example of an aquifer regeneration in an uranium mine. The ore was leached in this mine by in-situ leaching (ISL) using sulfuric acid. The hydrochemical composition of the water that is in the aquifer after this in-situ leaching process is shown as “ISL” in Table 40:

Table 40 Water analysis of a natural groundwater (GW) and groundwater influenced by in-situ leaching (ISL) (concentrations in mg/L)

Parameter	GW	ISL	Parameter	GW	ISL	Parameter	GW	ISL
pe	6.08	10.56	Cu	0.005	3	Ni	0.005	5
Temp.	10 °C	10	F	0.5	1	NO ₃ ⁻	0.5	100
Al	3.0	200	Fe	0.6	600	Pb	0.05	0.2
As	0.004	2	K	1.5	4	pH	6.6	2.3
C(4)	130		Li	0.02	0.1	Si	3.64	50
Ca	36.6	400	Mg	3.5	50	SO ₄ ²⁻	14.3	5000
Cd	0.0003	1	Mn	0.07	20	U	0.005	40
Cl	2.1	450	Na	5.8	500			

The simulation will be done in a zone of 200 m between an infiltration well and a pumping well. This zone shows a k_f value of $5 \cdot 10^{-5}$ m/s along the fracture and 10^{-8} m/s within the pores (those k_f values are only for orientation and are not needed directly for the modeling). The flow velocity is 10 m/day due to the potential head.

The dispersivity is 2 m. Natural groundwater (“GW” in Table 40) will be infiltrated in the infiltration well and extracted at the pumping well.

Assume that the exchange between pores and fractures only takes place by diffusion ($2 \cdot 10^{-10} \text{ m}^2/\text{s}$). The fracture volume is 0.05, and the pore volume is 0.15. Presuppose that the fractures are planar and that the distance between them is 20 cm. Thus, on average each fracture has a pore matrix of 10 cm thickness to each side. Homogeneous and heterogeneous reactions shall be ignored.

The simulation time is supposed to be 200 days. Thus, the water of the fractures will be exchanged 10 times in the 200 m long aquifer section.

The discretisation shall be carried out in elements of 10 m length. The connection of the immobile cells to the mobile cells is done by a box for each cell (Fig. 45) and the exchange between mobile and immobile cells by the means of a 1st order reaction (for theory see chapter 1.3.3.3.1). Present the concentrations of the elements U, Fe, Al, and S at the pumping well over a period of 200 days.

Change the parameter “immobile pore volume” from 0.15 to 0.05 and the matrix thickness on each side of each fracture from 0.1 to 0.01. Compare the results.

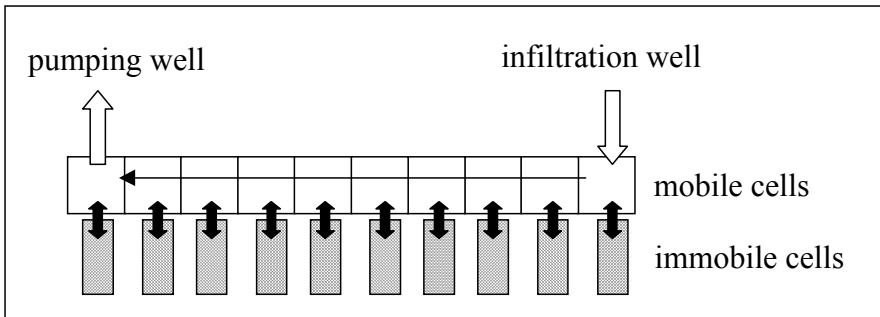


Fig. 45 Scheme for the model approach of a double porosity aquifer