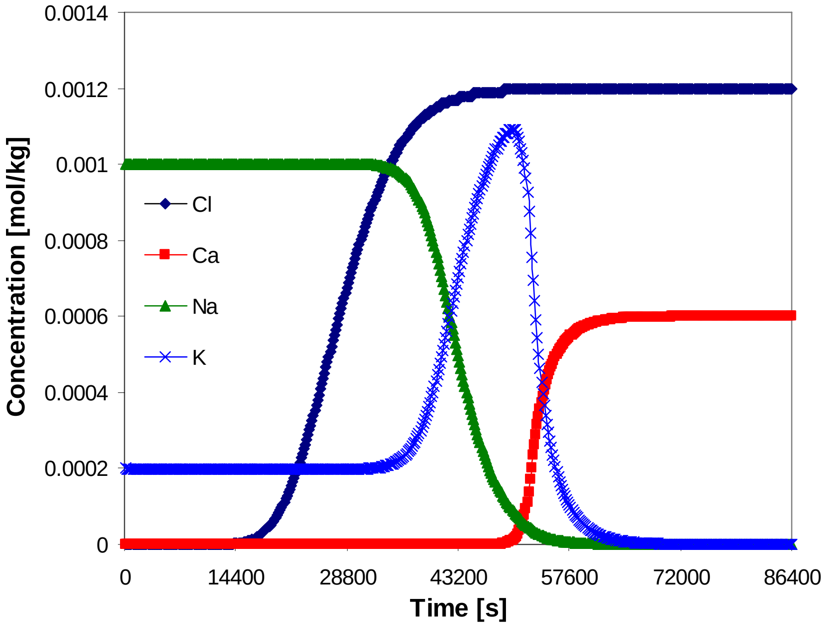
HP1 Tutorials II

(HYDRUS-1D + PHREEQC)



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List of Tutorials:

Abstract

Jacques, D., and J. Šimůnek, HP1 Tutorials II, PC Progress, Prague, Czech Republic, 2009.

The purpose of this short report is to documents four simple tutorials for the version 2.0 of HP1. HP1 is a comprehensive modeling tool in terms of available chemical and biological reactions that was recently developed by coupling HYDRUS-1D with the PHREEQC geochemical code of *Parkhurst and Appelo* [1999]. This coupling resulted in the very flexible simulator, HP1, which is an acronym for HYDRUS1D-PHREEQC [*Jacques and Šimůnek*, 2005; *Jacques et al.*, 2006]. The combined code contains modules simulating (1) transient water flow in variably-saturated media, (2) the transport of multiple components, (3) mixed equilibrium/kinetic biogeochemical reactions, and (4) heat transport. HP1 is a significant expansion of the individual HYDRUS-1D and PHREEQC programs by combining and preserving most or all of the features and capabilities of the two codes into a single numerical model. The code uses the Richards equation for variably-saturated flow and advection-dispersion type equations for heat and solute transport. However, the program can now simulate also a broad range of low-temperature biogeochemical reactions in water, the vadose zone and in ground water systems, including interactions with minerals, gases, exchangers, and sorption surfaces, based on thermodynamic equilibrium, kinetics, or mixed equilibrium-kinetic reactions. Various additional applications of HP1 were presented by [*Jacques and Šimůnek*, 2005, and *Jacques et al*., 2006, 2008a,b].

Four tutorials are currently presented in this report. The first tutorial involves the Transport and Dissolution of Gypsum and Calcite, the second and third tutorials the Transport and Cation Exchange during a single pulse and multiple pulses, respectively; and finally the fourth tutorial involves Horizontal Infiltration of Multiple Cations and Cation Exchange. More tutorials will be included in future versions of this brief report.

1. HP1 Tutorial 1: Transport and Dissolution of Gypsum and Calcite

Sulfate-free water is infiltrated in a 50-cm long homogeneous soil column under steady-state saturated flow conditions. The reactive minerals present in the soil column are calcite ($CaCO_3$) and gypsum ($CaSO_4.2H_2O$), both at a concentration of 2.176×10^{-2} mmol/kg soil.

Physical properties of the soil column are as follows:
Porosity = 0.35
Saturated hydraulic conductivity = 10 cm/day
Bulk density = 1.8 g/cm³
Dispersivity = 1 cm.

The input solution contains 1 mM $CaCl_2$ and is in equilibrium with the atmospheric partial pressure of oxygen and carbon dioxide. The initial soil solution is in equilibrium with the reactive minerals and with the atmospheric partial pressure of oxygen. As a result of these equilibria, the initial soil solution contains only Ca and oxidized components of S and C.

Calculate the movement of dissolution fronts of calcite and gypsum over a period of 2.5 days.

1.1. INPUT

Project Manager
Button: "New"
Name: "HP1-1"
Description: "Dissolution of calcite and gypsum in the soil profile"
Button: "OK"

Main Processes
Heading: Dissolution of calcite and gypsum in the soil profile
Uncheck: "Water Flow" (Note: this is a steady-state water flow)
Check: "Solute Transport"
Select: "HP1 (PHREEQC)"
Button: "Next"

Geometry Information
Depth of the Soil Profile: 50 (cm)
Button: "Next"

Time Information
Final Time: 2.5 (days)
Maximum Time Step: 0.05
Button: "Next"

Print Information
Unselect: T-Level information

Select: Print at Regular Time Interval
Time Interval: 0.025 (d)
Print Times: Number of Print times: 5
Button: "Next"

Print Times
Button: "Default"
Button: "OK"

HP1 – Print and Punch Controls
Check: "Make GNUplot Templates"

This allows easy visualization of time series and profile data for variables, which are defined in the `SELECTED_OUTPUT` section below in this dialog window and also defined later in the *Additional Output* part of the **Solute Transport – HP1 Definitions** dialog.

Button: "Next"

Water Flow – Iteration Criteria
Button: "Next"

Water Flow – Soil Hydraulic Model
Button: "Next"

Water Flow – Soil Hydraulic Parameters
Qs: 0.35
Ks: 10 (cm/d)
Button: "Next"

Water Flow – Boundary Conditions
Upper Boundary Condition: Constant Pressure Head
Lower Boundary Condition: Constant Pressure Head
Button: "Next"

Solute Transport – General Information
Stability Criteria: 0.25 (to limit the time step)
Number of Solutes: 6
Button: "Next"

Solute Transport – HP1 Components and Database Pathway
Six Components: Total_O, Total_H, Ca, C(4), Cl, S(6)

Note: Redox sensitive components should be entered with the secondary master species, i.e., with their valence state between brackets. The primary master species of a redox sensitive component, i.e., the element name without a valence state, is not recognized as a component to be transported. Therefore, the primary master species C can not be entered here; one has to enter either C(4) or C(-4). Also S is not allowed; one has to enter either

S(6) or S(-2). Note that the HYDRUS GUI will not check if a correct master species is entered. Because the redox potential is high in this example (a high partial pressure of oxygen), the secondary master species C(-4) and S(-2) are not considered.

Check: "Create PHREEQC.IN file using HYDRUS GUI"
Button: "Next"

Solute Transport – HP1 Definitions

Definitions of Solution Composition

Define the initial condition, i.e., the solution composition of water in the soil column, with the identifier 1001:

- Pure water
- Bring it in equilibrium with gypsum, calcite, and O(0), to be in equilibrium with the partial pressure of oxygen in the atmosphere

Define the boundary condition, i.e., the solution composition of water entering the soil column, with the identifier 3001:

- Ca-Cl solution
- Use pH to obtain the charge balance of the solution
- Adapt the concentration of O(0) and C(4) to be in equilibrium with the atmospheric partial pressure of oxygen and carbon dioxide, respectively

```
solution 1001
equilibrium_phases 1001
gypsum
calcite
O2(g) -0.68
save solution 1001
end

solution 3001
-units mmol/kgw
pH 7 charge
Cl 2
Ca 1
O(0) 1 O2(g) -0.68
C(4) 1 CO2(g) -3.5
```

Button: "OK"

Geochemical Model

Define for each node the geochemical model. Note that the initial amount of a mineral must be defined as mol/1000 cm³ soil (i.e., 2.176 x 10^{-5} mol/kg soil * 1.8 kg/1000 cm³).

```
Equilibrium_phases 1-101
gypsum 0 3.9E-5
calcite 0 3.9E-5
O2(g) -0.68
```

Button: "OK"

Additional Output

Define the additional output to be written to selected output files.

```
selected_output
 -totals Ca Mg Cl S C
 -equilibrium_phases gypsum calcite
```

Button: "OK"

Button: "Next"

Solute Transport – Solute Transport Parameters

Bulk D. = 1.8 (g/cm³)
Disp: 1 cm
Button: "Next"

Solute Transport – Boundary Conditions

Upper Boundary Condition	Bound. Cond. 3001

Soil Profile – Graphical Editor

Menu: Conditions -> Initial Conditions -> Pressure Head
Button: "Edit Condition"
    Select All
    Top Value: 0
Menu: Conditions -> Observation Points
Button: "Insert"
Insert 5 observation nodes, one for every 10 cm
Menu: File -> Save Data
Menu: File –> Exit

Soil Profile – Summary

Button: "Next"

Run Application

1.2. OUTPUT

The standard HYDRUS output can be viewed using commands in the right Post-Processing part of the project window. Only the total concentrations of the components, which were defined in “**Solute Transport – HP1 Components**” can be viewed using the HYDRUS-GUI.

HP1 creates a number of additional output files in the project folder. The path to the project folder is displayed in the Project Manager:

File -> Project Manager
Directory: gives the path to the project group folder
Input and output files of a given project are in the folder: *directory\project_name*

where *directory* is the project group folder
project is the project name

Following HP1 output files are created for the HP1-1 project:

Createdfiles.out	An ASCII text file containing a list of all files created by HP1 (in addition to the output files created by the HYDRUS module of HP1);
Phreeqc.out	An ASCII text file, which is the standard output file created by the PHREEQC-module in HP1;
HP1-1.hse	An ASCII text file, tab-delimited, that includes a selected output of all geochemical calculations in HP1 carried out before actual transport calculations. Inspection of this file can be done with any spreadsheet, such as MS Excel;
obs_nod_chem21.out *obs_nod_chem41.out* *obs_nod_chem61.out* *obs_nod_chem81.out* *obs_nod_chem101.out*	A series of ASCII files, tab-delimited, with the selected output for the defined observation nodes (21, 41, 61, 81, and 101) at specific times (every 0.025 days). Numerical values can be seen by opening this file in a spreadsheet, such as Excel. A single plot of time series at five observation nodes can be generated for each geochemical variable with the ts_*.plt files using the GNUPLOT graphical program (see below);
nod_inf_chem.out	An ASCII file, tab-delimited, with the selected output for a complete soil profile at the defined observation times. Numerical values can be seen by opening this file in a spreadsheet such as Excel. A single plot of the profile data at different observation times can be generated for each geochemical variable with the pd_*.plt files using GNUPLOT (see below);
ts_pH.plt *pd_pH.plt*	

ts_pe.plt	
pd_pe.plt	An ASCII file containing command line instructions to generate a plot of pH or pe using GNUPLOT;
ts_tot_Ca.plt	
pd_tot_Ca.plt	
ts_tot_Cl.plt	
pd_tot_Cl.plt	
ts_tot_S.plt	
pd_tot_S.plt	
ts_tot_C.plt	
pd_tot_C.plt	An ASCII file containing command line instructions to generate a plot with total concentrations of Ca, Cl, S and C using GNUPLOT; note that this information can also be viewed using the HYDRUS GUI;
ts_eq_gypsum.plt	
pd_eq_gypsum.plt	
ts_eq_calcite.plt	
pd_eq_calcite.plt	An ASCII file containing command line instructions to generate a plot with the amount of the minerals gypsum and calcite with GNUPLOT;
ts_d_eq_gypsum.plt	
pd_d_eq_gypsum.plt	
ts_d_eq_calcite.plt	
pd_d_eq_calcite.plt	An ASCII file containing command line instructions to generate a plot with the change in amount of the minerals gypsum and calcite with GNUPLOT;

To view these various plots, the GNUPLOT code needs to be installed on your computer. GNUPLOT is freeware software that can be downloaded from http://www.gnuplot.info/. Note that GNUPLOT (the wgnuplot.exe program for the Windows OS) is usually, after being downloaded, in the gnuplot\bin folder and does not require any additional special installation.

After opening the Windows version of GNUPLOT by clicking on wgnuplot.exe, a plot can be directly generated by carrying out these commands:

File->Open
Browse to the project folder
Open the template file of interest (*.plt)

The figure can be adapted using line commands (see tutorials on the internet). After adaptations, the command lines can be saved to be used later on.

The default terminal for the plots is Window. We illustrate here only how a plot can be transferred to another terminal:

```
Set terminal emf
```

```
Set output "name.emf"
Replot
Set terminal window
Replot
```

A *name*.emf file is created in the project directory.

1.3. Overview of Selected Results: Profile Data

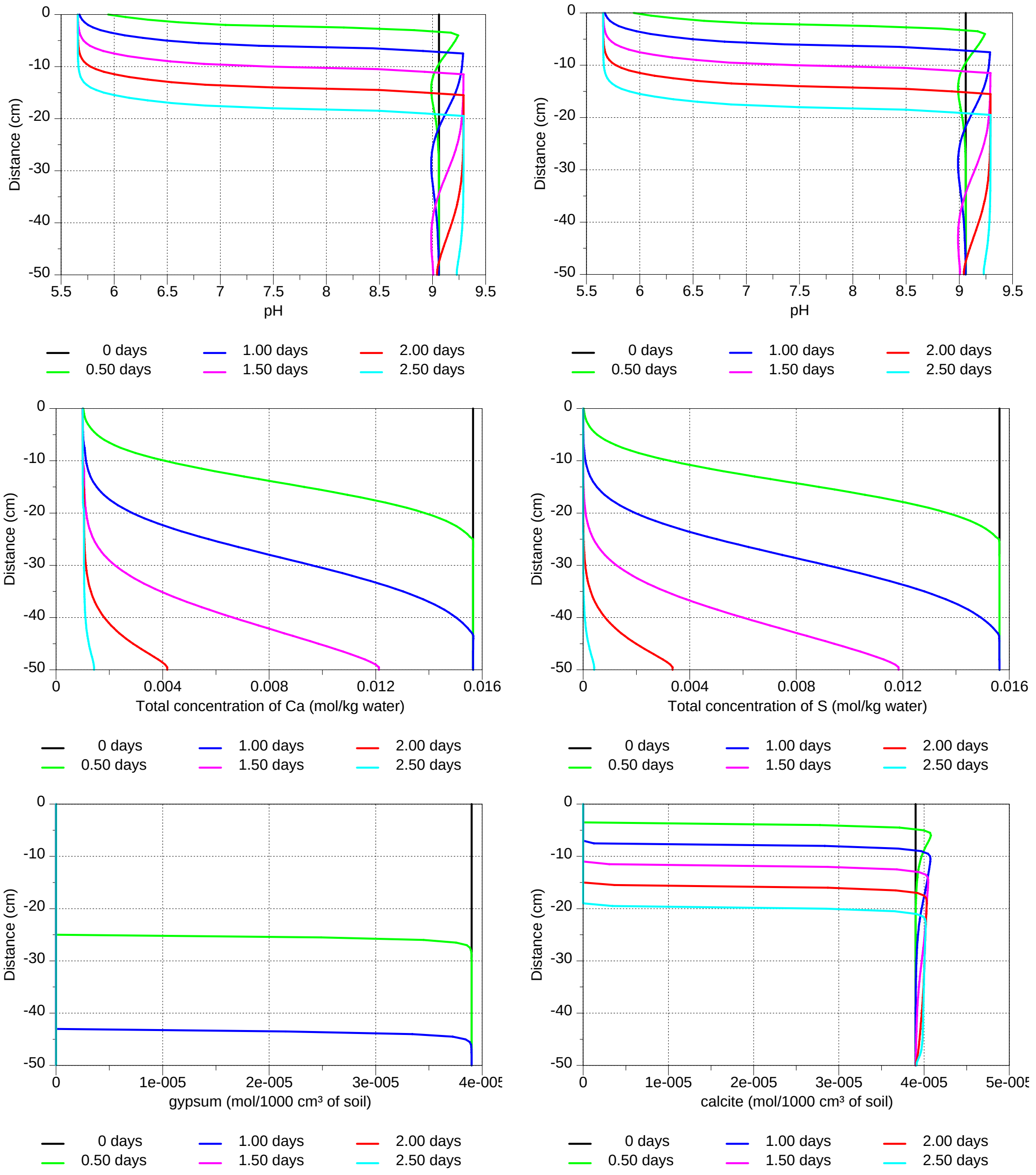

Figure 1. Profiles of pH (top left), total aqueous C concentration (top right), total aqueous Ca concentration (middle left), total aqueous S concentration (middle right), the amount of gypsum (bottom left) and the amount of calcite (bottom right) at selected print times during dissolution of calcite and gypsum.

1.4. Overview of Selected Results: Time Series

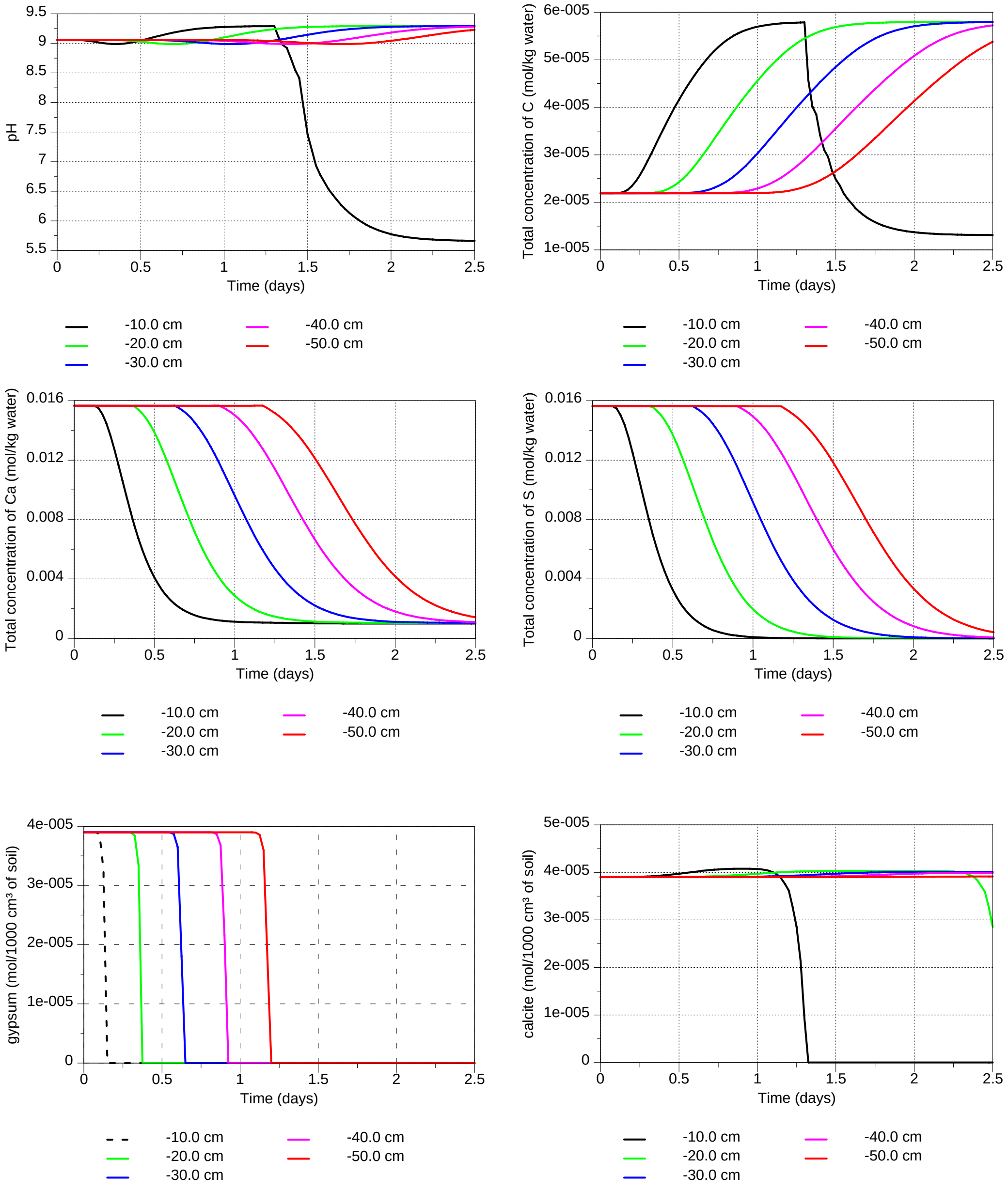

Figure 2. Time series of pH (top left), total aqueous C concentration (top right), total aqueous Ca concentration (middle left), total aqueous S concentration (middle right), the amount of gypsum (bottom left) and the amount of calcite (bottom right) at selected depths (observation nodes) during dissolution of calcite and gypsum.

2. HP1 Tutorial 2: Transport and Cation Exchange (a single pulse)

This example is adapted from Example 11 of the PHREEQC manual [*Parkhurst and Appelo*, 1999]. We will simulate the chemical composition of the effluent from an 8-cm column containing a cation exchanger. The column initially contains a Na-K-NO_3 solution in equilibrium with the cation exchanger. The column is flushed with three pore volumes of a $CaCl_2$ solution. Ca, K and Na are at all times in equilibrium with the exchanger. The simulation is run for one day; the fluid flux density is equal to 24 cm/d (0.00027777 cm/s).

The column is discretized into 40 finite elements (i.e., 41 nodes). The example assumes that the same solution is initially associated with each node. Also, we use the same exchanger composition for all nodes.

The initial solution is Na-K-NO_3 solution is made by using 1 x 10^{-3} M $NaNO_3$ and 2 x 10^{-4} M KNO_3 M. The inflowing $CaCl_2$ solution has a concentration of 6 x 10^{-4} M. Both solutions were prepared under oxidizing conditions (in equilibrium with the partial pressure of oxygen in the atmosphere). The amount of exchange sites (X) is 1.1 meq/1000 cm^3 soil. The log *K* constants for the exchange reactions are defined in the PHREEQC.dat database and do not have to be therefore specified at the input.

In this example, only the outflow concentrations of Cl, Ca, Na, and K are of interest.

2.1. INPUT

Project Manager

Button "New"
Name: CEC-1
Description: Transport and Cation Exchange, a single pulse
Button "OK"

Main Processes

Heading: Transport and Cation Exchange, a single pulse
Uncheck "Water Flow" (steady-state water flow)
Check "Solute Transport"
Select “HP1 (PHREEQC)”
Button "Next"

Geometry Information

Depth of the soil profile: 8 (cm)
Button "Next"

Time Information

Time Units: Seconds (Note that you can also just put it in days, this would also be OK)
Final Time: 86400 (s)

Initial Time Step: 180
Minimum Time Step: 180
Maximum Time Step: 180 (Note: constant time step to have the same conditions as in the original comparable PHREEQC calculations).
Button "Next"

Print Information
Number of Print Times: 12
Button "Select Print Times"
Button "Next"

Print Times
Button: "Default"
Button: "OK"

HP1 – Print and Punch Controls
Button: "Next

Water Flow - Iteration Criteria
Lower Time Step Multiplication Factor: 1
Button "Next"

Water Flow - Soil Hydraulic Model
Button "Next"

Water Flow - Soil Hydraulic Parameters
Catalog of Soil Hydraulic Properties: Loam
Qs: 1 (Note: to have the same conditions as in the original comparable PHREEQC calculations)
Ks: 0.00027777 (cm/s)
Button "Next"

Water Flow - Boundary Conditions
Upper Boundary Condition: Constant Pressure Head
Lower Boundary Condition: Constant Pressure Head
Button "Next"

Solute Transport - General Information
Number of Solutes: 7
Button "Next"

Solute Transport – HP1 Components and Database Pathway
Add seven components: Total_O, Total_H, Na, K, Ca, Cl, N(5)
Check: "Create PHREEQC.IN file Using HYDRUS GUI"
Button: "Next"

Solute Transport – HP1 Definitions

Definitions of Solution Composition

Define the initial condition 1001:

- K-Na-N(5) solution
- use pH to charge balance the solution
- Adapt the concentration of O(0) to be in equilibrium with the partial pressure of oxygen in the atmosphere

Define the boundary condition 3001:

- Ca-Cl solution
- Use pH to charge balance the solution
- Adapt the concentration of O(0) to be in equilibrium with the partial pressure of oxygen in the atmosphere

```
Solution 1001 Initial condition
 -units mmol/kgw
 pH 7 charge
 Na 1
 K 0.2
 N(5) 1.2
 O(0) 1 O2(g) -0.68

Solution 3001 Boundary solution
 -units mmol/kgw
 pH 7 charge
 Ca 0.6
 Cl 1.2
 O(0) 1 O2(g) -0.68
```

Geochemical Model

Define for each node (41 nodes) the geochemical model, i.e., the cation exchange assemblage X (0.0011 moles / 1000 cm^3) and equilibrate it with the initial solution (solution 1001).

```
EXCHANGE 1-41 @Layer 1@
 X 0.0011
 -equilibrate with solution 1001
```

Button: "OK"

Additional Output

Since output is required only for the total concentrations and such output is available in the automatically generated file *obs_node.out*, there is not need to define additional output.

Button: "Next"

Solute Transport - Transport Parameters

Bulk Density: 1.5 (g/cm^3)
Disp.: 0.2 (cm)
Button "Next"

Solute Transport - Boundary Conditions

Upper Boundary Condition: Concentration Flux
Add the solution composition number (i.e., 3001) for the upper boundary condition
Lower Boundary Condition: Zero Gradient
Button "Next"

Soil Profile - Graphical Editor

Menu: Conditions->Profile Discretization
or **Toolbar:** Ladder
Number (from sidebar): 41
Menu: Conditions->Initial Conditions->Pressure Head
or **Toolbar:** red arrow
Button "Edit condition", select with *Mouse* the entire profile and specify 0 cm pressure head.
Menu: Conditions->Observation Points
Button "Insert", Insert a node at the bottom
Menu: File->Save Data
Menu: File->Exit

Soil Profile - Summary

Button "Next"

Close Project

Run project

Note: This exercise will produce following warnings: "Master species N(3) is present in solution *n* but is not transported.". The same warning occurs for N(0). N(3) and N(0) are two secondary master species from the primary master species N. Only the secondary master species N(5) was defined as a component to be transported (Solute Transport – HP1 Components). HP1, however, checks if all components, which are present during the geochemical calculations, are defined in the transport model. If not, a warning message is generated. In our example, the concentrations of the components N(0) and N(3) are very low under the prevailing oxidizing conditions. Therefore, they can be neglected in the transport problem. If you want to avoid these warnings, you have to either include N(0) and N(3) as components to be transported or define an alternative primary master species representing nitrate (such as Nit^-) using `SOLUTION_MASTER_SPECIES` and `SOLUTION_SPECIES`.

2.2. OUTPUT

Display results for “Observation Points” or “Profile Information”. Alternatively, the **Figure 3** graph can be created using information in the output file *obs_nod.out*.

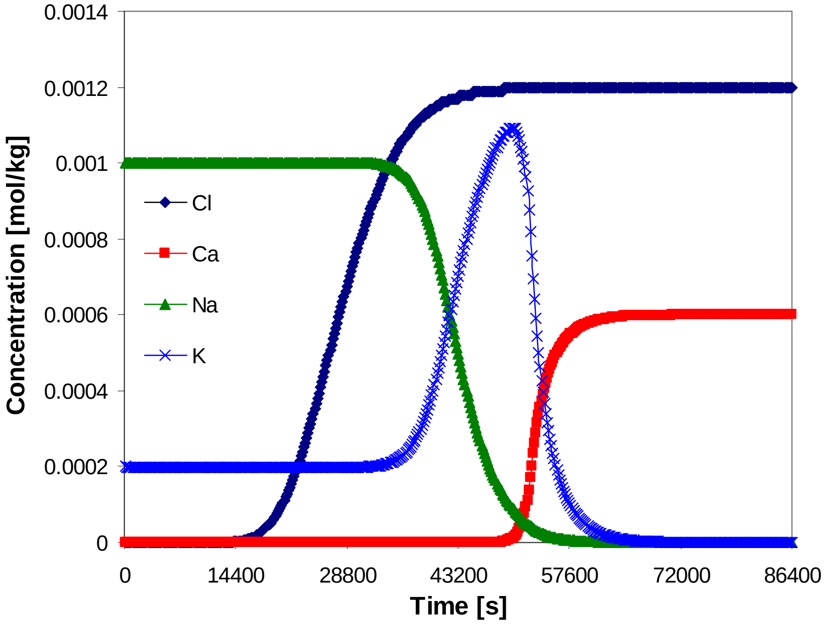

Figure 3. Outflow concentrations of Cl, Ca, Na and K for the single-pulse cation exchange example.

Results for this example are shown in **Figure 3**, in which concentrations for node 41 (the last node) are plotted against time. Chloride is a conservative solute and arrives in the effluent at about one pore volume. The sodium initially present in the column exchanges with the incoming calcium and is eluted as long as the exchanger contains sodium. The midpoint of the breakthrough curve for sodium occurs at about 1.5 pore volumes. Because potassium exchanges more strongly than sodium (larger log *K* in the exchange reaction; note that log *K* for individual pairs of cations are defined in the database and therefore did not have to be specified), potassium is released after sodium. Finally, when all of the potassium has been released, the concentration of calcium increases to a steady-state value equal to the concentration of the applied solution.

3. HP1 Tutorial 3: Transport and Cation Exchange (multiple pulses)

This example is the same as the one described in the previous example, except that time variable concentrations are applied at the soil surface.

Following sequence of pulses are applied at the top boundary:

0 – 8 hr: 6 x 10^{-4} M $CaCl_2$

8 – 18 hr: 5 x 10^{-6} M $CaCl_2$, 1 x 10^{-3} M $NaNO_3$, and 2 x 10^{-4} M KNO_3

18 – 38 hr: 6 x 10^{-4} M $CaCl_2$

38 – 60 hr: 5 x 10^{-6} M $CaCl_2$, 1 x 10^{-3} M $NaNO_3$, and 8 x 10^{-4} M KNO_3

3.1. INPUT

Project Manager

Click on **CEC-1**
Button "Copy"
New Name: CEC-2
Description: Transport and Cation Exchange, multiple pulses
Button "OK", "Open"

Main Processes

Heading: Transport and Cation Exchange, multiple pulses
Button "Next"

Geometry Information

Button "Next"

Time Information

Time Units: hours
Final Time: 60 (h)
Initial Time Step: 0.1
Minimum Time Step: 0.1
Maximum Time Step: 0.1
Check Time-Variable Boundary Conditions
Number of Time-Variable Boundary Records: 4
Button "Next"

Print Information

Number of Print Times: 12
Button "Select Print Times"
Default
Button "OK"
Button "Next"

Solute Transport – HP1 Definitions

Definitions of Solution Composition

Add additional boundary solution compositions with numbers 3002 and 3003.
Define a bottom boundary solution: Solution 4001 – pure water

```
Solution 3002 Boundary solution
 -units mmol/kgw
 ph 7 charge
 Na 1
 K 0.2
 N(5) 1.2
 Ca 5E-3
 Cl 1E-2
 O(0) 1 O2(g) -0.68

Solution 3003 Boundary solution
 -units mmol/kgw
 ph 7 charge
 Na 1
 K 0.8
 N(5) 1.8
 Ca 5E-3
 Cl 1E-2
 O(0) 1 O2(g) -0.68

solution 4001 bottom boundary solution
 #pure water
```

Button: "OK"

Button: "Next"

Time-Variable Boundary Conditions

Fill in the time, and the solution composition number for the top boundary

Time	*cTop*	*cBot*
8	3001	4001
18	3002	4001
38	3001	4001
60	3003	4001

Soil Profile - Graphical Editor

Menu: Conditions->Observation Points
Button "Insert", Insert node at 2, 4, 6, and 8 cm
Menu: File->Save Data
Menu: File->Exit

Soil Profile - Summary

Button "Next"

Calculations - Execute HP1

3.2. OUTPUT

After the program finishes, explore the output files.

Figure 4 gives the K concentration at different depths in the profile. **Figure 5** shows the outflow concentration. The first pulse is identical to the single pulse project. Then additional solute pulses of different solution compositions will restart the cation exchange process depending on the incoming solution composition.

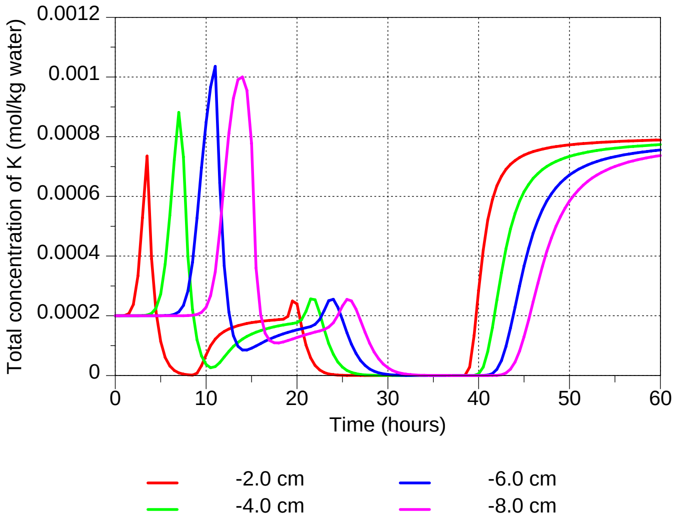

Figure 4. Time series of K concentrations at four depths for the multiple-pulse cation exchange example.

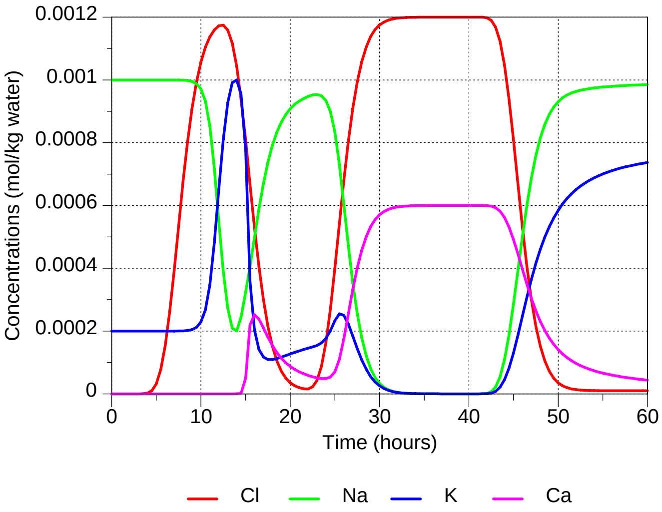

Figure 5. Outflow concentrations for the multiple-pulse cation exchange example.

4. HP1 Tutorial 4: Horizontal Infiltration of Multiple Cations and Cation Exchange

This exercise simulates horizontal infiltration of multiple cations (Ca, Na, and K) into the initially dry soil column. It is vaguely based on experimental data presented by *Smiles and Smith* [2004]. The cation exchange between particular cations is described using the Gapon Exchange equation [*White and Zelazny*, 1986]. For an exchange reaction on an exchange site X involving two cations N and M with charge *n* and *m*:

$$\mathrm{N}_{1/n}\mathrm{X} + 1/m\ \mathrm{M} = \mathrm{M}_{1/m}\mathrm{X} + 1/n\ \mathrm{N} \tag{1}$$

the Gapon selectivity coefficient $K_{\mathrm{G}MN}$ is:

$$K_{GMN} = \frac{\left[M_{1/m}X\right]\left[N^{n+}\right]^{1/n}}{\left[N_{1/n}X\right]\ \left[M^{m+}\right]^{1/m}} \tag{2}$$

where [] denotes activity. The activity of the exchange species is equal to its equivalent fraction. The Gapon selectivity coefficients for Ca/Na, Ca/K and Ca/Mg exchange are $K_{\mathrm{GCaNa}} = 2.9$, $K_{\mathrm{GCaK}} = 0.2$, and $K_{\mathrm{GCaMg}} = 1.2$. It is assumed that the cation exchange capacity c_T ($\mathrm{mol_c kg^{-1}}$ soil) is constant and independent of *p*H.

Consider a soil column 20-cm long with an initial water content of 0.075. Infiltration occurs on the left side of the column under a constant water content equal to the saturated water content. Consider a free drainage right boundary condition.

Some physical parameters of the column are: bulk density = 1.75 g/cm³ ; dispersivity = 10 cm ; the soil water retention characteristic and unsaturated hydraulic conductivity curve are described with the van Genuchten – Mualem model [*van Genuchten*, 1980] with following parameters: $\theta_s = 0.307$, $\theta_r = 0$, $\alpha = 0.259$ cm^{-1} , $n = 1.486$, $K_s = 246$ cm / day, and $l = 0.5$. The CEC is 55 meq/kg soil.

As initial concentrations take: [Cl] = 1 mmol/kg water, [Ca] = 20 mmol/kg water, [K] = 2 mmol/kg water, [Na] = 5 mmol/kg water, [Mg] = 7.5 mmol/kg water, and [C(4)] = 1 mmol/kg water. The pH is 5.2, and the solution contains an unknown concentration of $\mathrm{SO_4^{2-}}$ as a major anion. The inflowing solution has the following composition: [Ca] = 0.002345 mol/kg water, [Na] = 0.01 mol/kg water, [K] = 0.0201 mol/kg water, [Mg] = 0, and [Cl] = 0.035 mol/kgw. The pH is 3.2, and the solution contains an unknown concentration of $\mathrm{SO_4^{2-}}$ as a major anion.

Look at profile data of the water content, pH, concentrations of the cations and anions, and amounts of sorbed cations. Express sorbed concentrations in meq/kg soil.

4.1. DEFINITION OF THE GEOCHEMICAL MODEL AND ITS PARAMETERS

1. The CEC should be expressed in mol/1000 cm^3 soil in HP1. Recalculate the amount of CEC.

   [*Answer*: 0.09625 *mol / 1000 cm³ soil*]

2. Define the thermodynamic data for describing the exchange process with the Gapon convention and the Gapon selectivity coefficients.

   A new master exchange species has to be defined, say G.

   The exchange reactions (Eq. 1) have to be written in terms of half reactions:

```
G- + K+ = KG                    (3)
G- + Na+ = NaG                  (4)
G- + 0.5 Ca+2 = Ca0.5G          (5)
G- + 0.5 Mg+2 = Mg0.5G          (6)
```

   with appropriate values of the exchange coefficients. Thus, log K_{GK}, log K_{GNa}, log K_{GCa}, and log K_{GMg} are needed for equations 3, 4, 5, and 6, respectively. It is assumed that the log K_G value for the half reaction with Na is 1, i.e., log $K_{GNa} = 0.0$. The thermodynamic constants for the other half reactions can then be calculated from the defined Gapon selectivity coefficients.

   Calculate log K_{GK}, log K_{GCa}, and log K_{GMg}.

   Solution:

   Exchange reactions are written in terms of half reactions. The reaction:

   $\text{Na-G} + 0.5\ \text{Ca}^{2+} = \text{Na}^+ + \text{Ca}_{0.5}\text{-G} \quad K_{GCaNa}$

   can be written as the sum of two half reactions:

   (1) $\text{G}^- + \text{Na}^+ = \text{Na-G} \quad K_{GNa}$
   (2) $\text{G}^- + 0.5\ \text{Ca}^{2+} = \text{Ca}_{0.5}\text{-G} \quad K_{Gca}$

   Consequently:

   $\log(K_{GCaNa}) = \log(K_{GCa}) - \log(K_{GNa})$

   We express the exchange coefficients relative to Na^+. Thus, taking $\log(K_{GNa})$ equals to 0, $\log(K_{GCa}) = \log(K_{GCaNa})$. Similarly, for the reaction:

   $\text{K-G} + 0.5\ \text{Ca2}^+ = \text{K}^+ + \text{Ca}_{0.5}\text{-G} \quad K_{GCaK}$

the following two half reactions can be written:

(1) $G^- + K^+ = K\text{-}G$ $\quad K_{GK}$
(2) $G^- + 0.5\ Ca^{2+} = Ca_{0.5}\text{-}G$ $\quad K_{Gca}$

Then, $\log(K_{GCaK}) = \log(K_{GCa}) - \log(K_{GK})$. And similarly, $\log(K_{GK}) = \log(K_{GCa}) - \log(K_{GCaK})$. The same reasoning is applied also to derive K_{GMg}.

[*Answer*: Log $K_{GK} = 1.16$
Log $K_{GCa} = 0.462$
Log $K_{GMg} = 0.383$]

4.2. INPUT

Project Manager
Button "New"
Name: CEC-3
Description: Horizontal Infiltration with Cation Exchange
Button "OK"

Main Processes
Heading: Horizontal Infiltration with Cation Exchange
Check "Water Flow"
Check "Solute Transport"
Select “HP1 (PHREEQC)”
Button "Next"

Geometry Information
Depth of the soil profile: 20 (cm)
Decline from vertical axes: 0 (horizontal flow)
Button "Next"

Time Information
Time Units: Minutes
Final Time: 144 (min)
Initial Time Step: 0.01
Minimum Time Step: 0.01
Maximum Time Step: 2
Button "Next"

Print Information
Number of Print Times: 6
Button "Select Print Times"
Button "Default(log)"
Button "OK"

Button "Next"

HP1 – Print and Punch Controls

Select: Make GNUPLOT templates
Button: "Next

Water Flow - Iteration Criteria

Lower Time Step Multiplication Factor: 1.3
Button "Next"

Water Flow - Soil Hydraulic Model

Button "Next"

Water Flow - Soil Hydraulic Parameters

Catalog of Soil Hydraulic Properties: Loam
Qr: 0
Qs: 0.307
Alpha: 0.259 (cm^{-1})
n: 1.486
Ks: 0.170833 (cm/min)
Button "Next"

Water Flow - Boundary Conditions

Initial Conditions: in Water Contents
Upper Boundary Condition: Constant Water Content
Lower Boundary Condition: Free Drainage
Button "Next"

Solute Transport - General Information

Number of Solutes: 9
Button "Next"

Solute Transport – HP1 Components and Database Pathway

Add the nine components: Total_O, Total_H, Ca, Na, K, Mg, Cl, C(4), S(6)
Check: "Create PHREEQC.IN file using HYDRUS GUI"
Button: "Next"

Solute Transport – HP1 Definitions

Additions to Thermodynamic Database

- Define the master exchange species G
- Define the master species. An identical reaction for the master exchange species has to be included.

```
EXCHANGE_MASTER_SPECIES
G G-
```

```
EXCHANGE_SPECIES
G- = G-; log_k 0
G- + K+ = KG; log_k 1.16
G- + Na+ = NaG; log_k 0
G- + 0.5 Ca+2 = Ca0.5G; log_k 0.462
G- + 0.5 Mg+2 = Mg0.5G; log_k 0.383
```

Button: "OK"

Definitions of Solution Compositions

- Define the initial solution as solution 1001
- Define the boundary solution as solution 3001
- Assume that the solutions are in equilibrium with the partial pressure of oxygen and carbon dioxide of the atmosphere

```
solution 1001 initial solution
pH 5.2
Cl 1
Ca 20
K 2
Na 5
Mg 7.5
C(4) 1 CO2(g) -3.5
O(0) 1 O2(g) -0.68
S(6) 1 charge

solution 3001 boundary solution
pH 3.2
Ca 2.345
Na 10
K 20
Cl 35
C(4) 1 CO2(g) -3.5
O(0) 1 O2(g) -0.68
S(6) 1 charge
```

Button: "OK"

Geochemical Model

- Define an exchange assemblage for 101 nodes
- Equilibrate the exchange site with the initial solution

```
Exchange 1-101
G 0.09625
-equilibrate with solution 1001
```

Button: "OK"

Additional Output

- Add `SELECTED_OUTPUT` to ask for output of total concentrations of the components
- Add `USER_PUNCH` to save the absorbed concentrations as meq/kg soil. The default output in HP1 for an exchange species is mol/kg water. This can be asked by `-molalities` NaG in `SELECTED_OUTPUT` or as a basic statement (10 punch mol("NaG")) in `USER_PUNCH`. Basic statements to convert 'mol/kg water' to 'meq/kg soil' can be added to `USER_PUNCH`. The following two variables are needed:
    - The bulk density: use the HP1-specific BASIC statement bulkdensity(*number*), where *number* is the cell number of a given node, to obtain the bulk density for a given node. The number of the cell is obtained by the BASIC statement cell_no.
    - The water content: obtained as tot("water").
- Add meaningful headings for the punch output.

```
SELECTED_OUTPUT
 -totals Cl Ca K Na Mg S

USER_PUNCH
-headings Sorbed_Ca@meq/kg_soil Sorbed_Mg@meq/kg_soil
Sorbed_Na@meq/kg_soil Sorbed_K@meq/kg_soil
-start
 10 bd = bulkdensity(cell_no) #kg/1000cm³ soil
 40 PUNCH mol("Ca0.5G")*tot("water")/bd*1000 #in meq/kg
 50 PUNCH mol("Mg0.5G")*tot("water")/bd*1000 #in meq/kg
 60 PUNCH mol("NaG")   *tot("water")/bd*1000 #in meq/kg
 70 PUNCH mol("KG")    *tot("water")/bd*1000 #in meq/kg
-end
```

Button: "OK"

Button: "next"

Solute Transport – Solute Transport Parameters

Bulk Density: 1.75 (g/cm^3)
Disp: 10 (cm)
Button "Next"

Solute Transport - Boundary Conditions

Upper Boundary Condition: Concentration Flux
Bound. Cond.: 3001
Lower Boundary Condition: Zero Gradient
Button "Next"

Soil Profile - Graphical Editor

Menu: Conditions -> Initial Conditions -> Water content
Button: "Edit Condition"
Select All

Top Value: 0.075
Button: "Edit Condition"
Select first node
Value: 0.307
Menu: Conditions -> Observation Points
Button: "Insert"
Insert 4 observation nodes at 3, 6, 9, and 12 cm
Menu: File -> Save Data
Menu: File –> Exit

Soil Profile - Summary

Button "Next"

Calculations - Execute HP1

4.3. OUTPUT

Explore the HYDRUS output and the GNUPLOT templates.

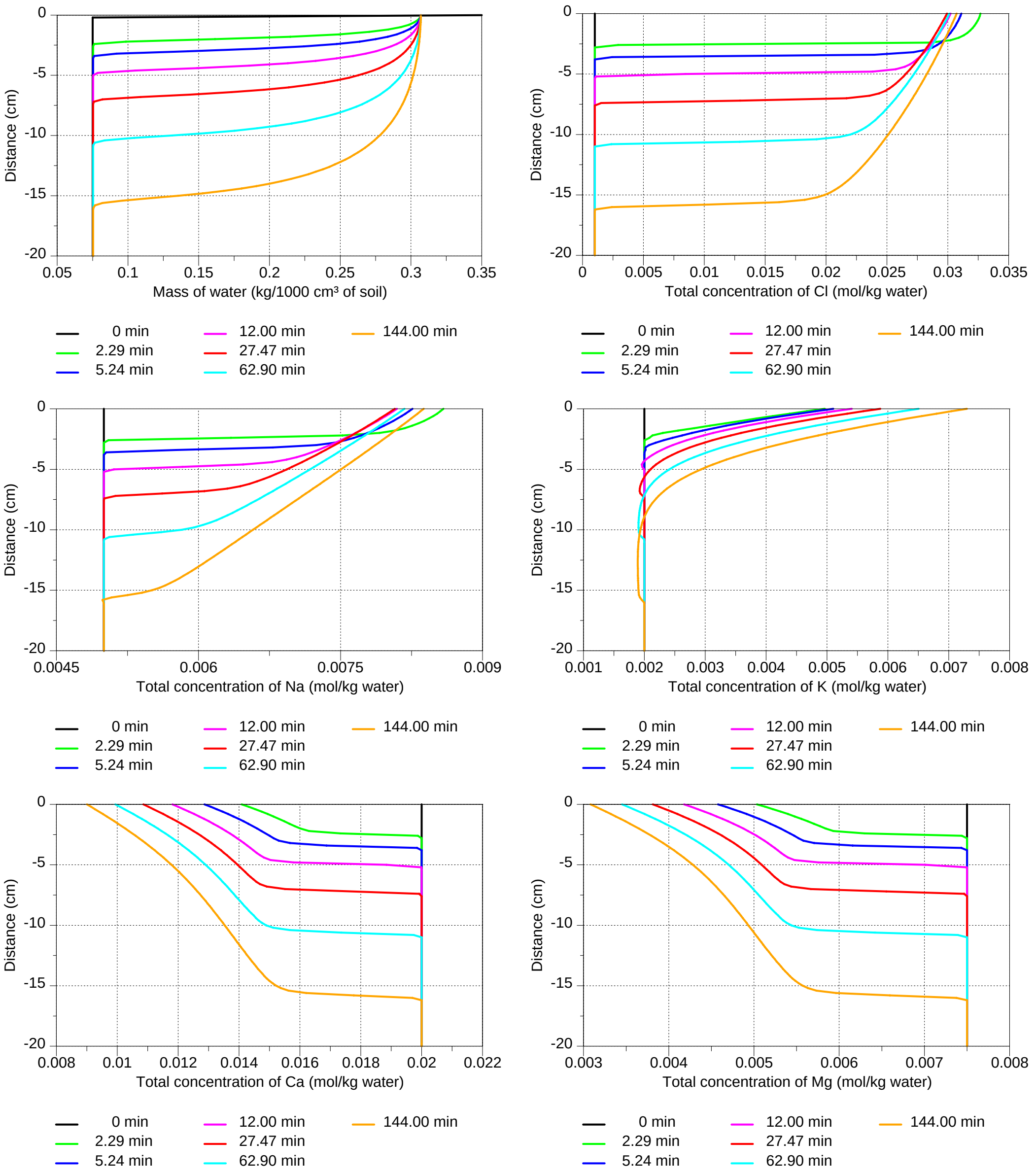

Figure 6. Profiles of water content (top left), and total aqueous concentrations of Cl, K, Na, K, Ca and Mg at selected times during horizontal infiltration of multiple cations.

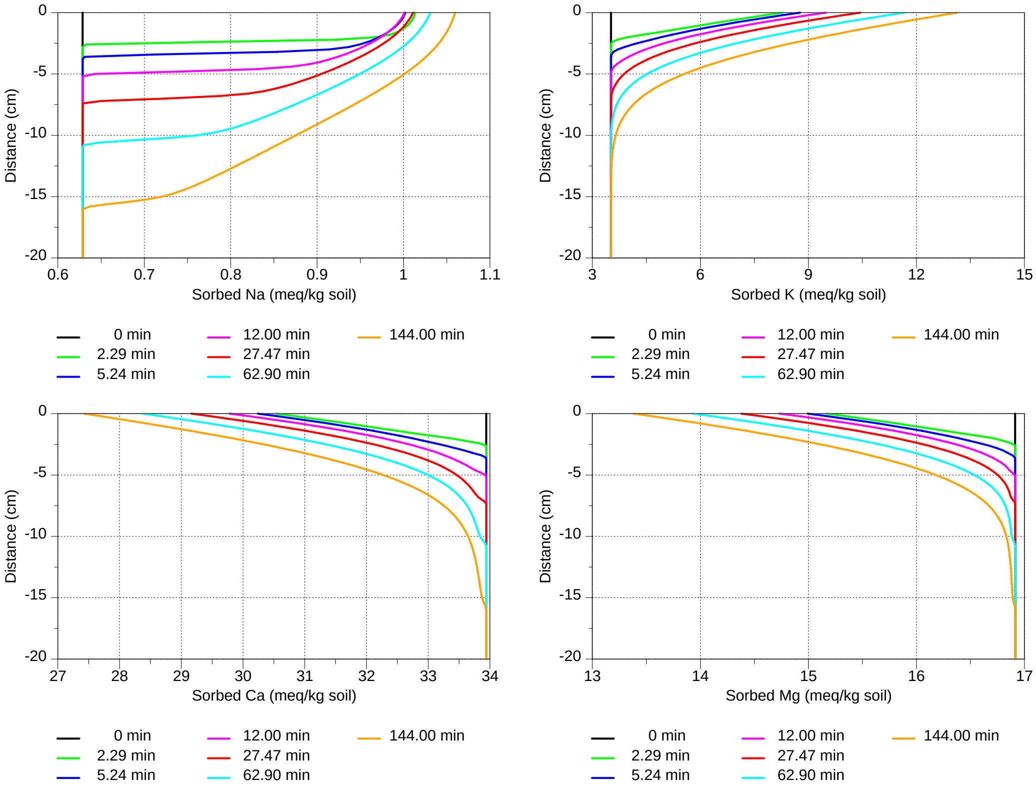

Figure 7. Profiles of sorbed concentrations of Na, K, Ca and Mg at selected times during horizontal infiltration of multiple cations.

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