第47回 農業農村工学会 土壌物理研究部会 研究集会

HYDRUS-1D の新機能の紹介と今後の展開



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主催:農業農村工学会土壌物理研究部会

会場:三重大学 三翠ホール

目 次

1. HYDRUS-1Dの新機能とその適用事例(演習) ー土中液状水・水蒸気・熱同時移動ー

斎藤広隆 …………1 東京農工大学

カリフォルニア大学リバーサイド校 坂井勝

2. 多成分化学物質移動予測プログラム HP1 の概要

三重大学 取出伸夫·陳代文·Dimitar Antonov ······16

3. HP1を用いた形態変化を伴う土中の窒素移動(演習)

三重大学 取出伸夫·Dimitar Antonov ·········26

4. マルチステップ法による水分移動特性の推定

鳥取大学 井上光弘 ······105

5. 負圧浸入計による表層土の水分移動特性の推定

東京農工大学大学院連合農学研究科 朝田景 …………125

部会の歴史

規約

 Outline Example 1. Steady-state flow and transport of linearly adsorbed contaminant (STADS) Example 2. Steady-state flow and cation exchange (CATEX) Example 3. Steady-state flow and transport of linearly adsorbed contaminant with first-order chain degradation (DEGRAD) Example 4. Steady-state flow and transport of linearly adsorbed organic nitrogen with first-order degradation and cation exchange processes (NITROG) 		Example 1. STADS • Cheneral governing transport equation for linearly adsorbing chemicals (with no degradation) is: $R \frac{\partial c_{i,i}}{\partial t} = \frac{\partial}{\partial t} \left(D_i^* \frac{\partial c_{i,i}}{\partial x} \right) - \frac{g}{\theta} \frac{\partial c_{i,i}}{\partial x}$ where R is the retardation factor equal to: $R = 1 + \frac{\rho_b K_d}{\theta}$ and K _d is the distribution coefficient [L ³ M ⁻¹], equal to: $c_a = K_d c_l$
Nitrogen transport modeling steps with HP1 modeling steps with HP1 Computer Session with Four Basic Examples Nobuo Toride, Dimitar Antonov, Daiwen Chen Mie University	Irrigation & Drainage Society, Soil Physics Meeting October 19, 2008	Example 1. STADS • Ceneral Information: • Ceneral Information: • Steady-state water flow ($q = 1 \text{ cm/d}$) • Time of simulation: 100 days • Time of simulation: 100 days • Soil profile 100 cm with bulk density 1.5 g/cm ³ , water content 0.5, solute dispersivity 1 cm (molecular diffusion = 0) • Component Cont with inflow concentration 0.01 mol/1 • Adsorption description: Freundlich type linear adsorption with distribution coefficient $K_d = 5 \text{ cm}^3/g$

Example 1. STADS	• Modeling linear adsorption in PHREEQC : Surface complexation reaction: Surface complexation reaction: where Sor is the adsorptive surface and SorCont is the adsorbed component. Where Sor is the adsorptive surface and SorCont is the adsorbed component. Applying <i>the law of mass action</i> assuming [Sor] is very large (= 1E+100 [mol/1]) gives: $K = \frac{[SorCont]}{[Sor]c_i} = \frac{c_a}{[Sor]c_i} = \frac{K_d\rho_b c_i}{[Sor]c_i} = \frac{10^{23}}{[Sor]}$ Since c_a is small, [Sor] remains almost constant regardless of c_a . $c_a = K[Sor]c_i \approx K_d\rho_b c_i$	NeuronNameNam<
Example 1. STADS	• The general governing transport equation in HP1 is: $\frac{\partial c_{i,i}}{\partial t} = \frac{\partial}{\partial x} \left(D^{w} \frac{\partial c_{i,i}}{\partial x} \right) - \frac{\partial}{\theta} \frac{\partial c_{i,i}}{\partial x} + R_{i}$ where R_{i} represents the source/sink due to geochemical reactions where R_{i} represents the source/sink due to geochemical reactions => The transport equation for adsorbing chemical is: $\frac{\partial c_{i,i}}{\partial t} = \frac{\partial}{\partial x} \left(D^{w} \frac{\partial c_{i,i}}{\partial x} \right) - \frac{\partial}{\theta} \frac{\partial c_{i,i}}{\partial t} - \frac{\partial_{x}}{\theta} \frac{\partial c_{u,i}}{\partial t}$ where considering Freundlich type linear adsorption: $c_{a} = K_{a}c_{l}$	Initial conditions at $t = t_i$ \clubsuit $C_i = c_i + K_a c_i$ Start a new time step Start a new time step $f = t_{i+1}$ Start a new time step $t = t_{i+1}$ Start a new time step $f = t_{i+1}$ Solute transport (no reaction) $\clubsuit c_{i+1}^{0} (\Delta c = c_{i+1}^{0} - c_i)$ Solute transport (no reaction) $\clubsuit c_{i+1}^{0} (\Delta c = c_{i+1}^{0} - c_i)$ $f = c_{i+1}^{0} + K_a c_i$ $\Rightarrow c_{i+1}^{1} = c_{i+1}^{1} + K_a c_i$ new equilibrium $f = t_{i+1}^{1} + K_a c_i$

Example 1. Highlights Input data: HYDRUS-ID Input data: HID Input data: HID

Example 1. Highlights Defining new element /not in the database/ (e.g., Cont) Defining new element /not in the database/ (e.g., Cont) $248708524470800202_{44709}(e.g., Cont) 24870810202_{44709}(e.g., Cont)0 = 0 = the available folder (e.g., Notepad etc.)0 = 0 = the the new element Cont as shown below:\int \frac{1}{26} \int \frac{1}{26}$	Example 2. CATEX Ceneral Information: • General Information: • Steady-state water flow ($q = 1 \text{ cm/d}$) • Time of simulation: 100 days Soil profile 100 cm with bulk density 1.5 g/cm ³ , water content 0.5, solute dispersivity 1 cm (molecular diffusion = 0) • Na-K-Cl (sodium-porassium-chloride) initial solution • Na-K-Cl (sodium-porassium-chloride) initial solution • Cation exchange capacity CEC = 0.73 mmol/kg soil • Cation exchange capacity cec = 0.73 mmol/kg soil
$\frac{\nabla c_{1AA}}{\partial r} = \frac{c}{\partial x} \left(D_{NA}^{w} \frac{\nabla c_{1AA}}{\partial x} \right) - \frac{q}{\theta} \frac{\nabla c_{1A}}{\partial x} + R_{NA} \qquad \frac{\nabla c_{1A}}{\partial r} = \frac{c}{\partial x} \left(D_{w}^{w} \frac{\nabla c_{1A}}{\partial x} + R_{w} \right)$ where R_{CA} , R_{CP} , R_{Na} and R_{K} represent the specific sink term due to the cation exchange interactions	with equilibrium constant: $k_{cak} = \frac{[cax 2]^{as} [k^+]}{[xx] [ca^{2s}]^{as}}$ (<i>iii</i>) $K^+ + Na-X \leftrightarrow K-X + Na^+$ with equilibrium constant: $k_{k'ab} = \frac{[kx] [Na^+]}{[Nax] [k^+]}$ where X represents the amount of the exchange sites (equal to CEC)



Example 3. DEGRAD	 Modeling first-order degradation rate in PHREEQC : 	 RATES (# keyword data block) Contadegradation -start 	 10 rem parm(1) first-order degradation coefficient (d-1) 20 rate=parm(1)*tot("water")*mol("Conta") 30 moles=-rate*time 40 save moles -end 	Example 3. DEGRAD	<figure><figure><figure></figure></figure></figure>
Example 3. DEGRAD	 First-order degradation rate equations: 	$rac{dConta}{dt} = -\mu_{cons}Conta$ $rac{dConta}{dt} = -\mu_{cons}Contb$	$\frac{dContc}{dt} = -\mu_{conc}Contc}$ where μ_i is the first-order degradation constant for the i^{th} component [T-1]	Example 3. DEGRAD	 Modeling first-order degradation rate in PHREEQC : KINETICS 1-101 (# keyword data block) Contadegradation formula Conta 1.0 Contb -1.0 formula Conta 1.0 Contb -1.0 parms 0.02



Example 4. NITROG	Example 4. NITROG
• First-order rate equations: $\frac{dOrg-N}{dt} = -\mu_{Org-N}Org-N$ $\frac{dNH_{4}^{+}}{dt} = -\mu_{NH_{4}^{+}}NH_{4}^{+} + \mu_{Org-N}Org-N$ $\frac{dNO_{3}}{dt} = -\mu_{NO_{3}^{-}}NO_{3}^{-} + \mu_{NH_{4}^{-}}NH_{4}^{+}$	• Cation exchange equation(s): $nNH_4^+ + Cation-X_n = nNH4-X + Cation^{n+}$ with equilibrium constant: $\kappa_{NH4Cation} = \frac{[NH4+X]^n}{[Cation-X_n][NH4^+]^n}$
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HP 1 (a coupled numerical code of the HYDRUS 1D and PHREEQC-2 programs)

EXAMPLE 1 (STADS)

Problem: Transport of linearly adsorbed solute with steady-state water flow (STADS) **Purpose:** Understanding the role of the HYDRUS and PHREEQC modules

General Information: We consider transport of single linearly adsorbed component (*Cont*) under saturated steady-state water flow through a soil column of 100 cm length for 100 days. The soil has 1.5 g/cm³ bulk density, and the saturated volumetric water content is 0.5. Water flux is 1 cm/d and inflow concentration of *Cont* is 0.01 mol/l (0.01 mmol/cm³). Solute dispersivity is 1 cm, assuming no molecular diffusion. The distribution coefficient for linear adsorption K_d is 5 cm³/g.

Governing equations: The one-dimensional solute transport equation for adsorbing chemicals without decay under steady-state water flow can be written as:

$$\frac{\partial c_{l,i}}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial c_{a,i}}{\partial t} = \frac{\partial}{\partial x} \left(D_i^w \frac{\partial c_{l,i}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial c_{l,i}}{\partial x}$$
(1)

where $i (= 1,...N_m)$ is the aqueous species number $(N_m$ is the total number of aqueous species), $c_{a,i}$ is the adsorbed concentration of the i^{th} species $[MM^{-1}]$, ρ_b is the bulk density $[ML^{-3}]$, $c_{l,i}$ is the aqueous concentration phase of the i^{th} species $[ML^{-3}]$, θ is the volumetric water content $[L^3L^{-3}]$, q is the water flux $[LT^{-1}]$ and D_i^w is the dispersion coefficient for the i^{th} species (L^2T^{-1}) .

In HP 1, the equation for the same problem has the form:

$$\frac{\partial C_{l,i}}{\partial t} = \frac{\partial}{\partial x} \left(D^w \frac{\partial C_{l,i}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,i}}{\partial x} + R_i$$
(2)

where $C_{l,i}$ is the total dissolved concentration of the *i*th species, and R_i is the general source/sink term due to geochemical reactions for the *i*th species [ML⁻³T⁻¹]. This sink/source term R_i indicates heterogeneous (between two different phases, e.g. solid – solute) equilibrium reactions and homogeneous (between same phases, e.g. solute – solute) and heterogeneous kinetic reactions. In case of adsorbing chemicals, the rate of adsorption (the second term of the right side of Eq.(1)) becomes the sink term:

$$\frac{\partial C_{l,i}}{\partial t} = \frac{\partial}{\partial x} \left(D^w \frac{\partial C_{l,i}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,i}}{\partial x} - \frac{\rho_b}{\theta} \frac{\partial C_{a,i}}{\partial t}$$
(3)

If adsorption is instantaneous and described with the linear Freundlich equation:

$$C_{a,i} = K_d C_{l,i} \tag{4}$$

where K_d is the distribution coefficient [L³M⁻¹].

Linear adsorption in PHREEQC: As the PHREEQC solves the tasks on the base of thermodynamic equilibrium or kinetic reaction equations, we express the linear adsorption process as a thermodynamic equilibrium equation. In PHREEQC, since all the concentration is given per unit volume of water, Eq. (4) is rewritten in terms of the amount adsorbed per unit volume of water:

$$C_{a,i}^{W} = K_{d} \rho_{b} C_{l,i} = K_{d}^{W} C_{l,i}$$
(5)

where K_d^w is the adsorption constant in mass per unit volume of water. Eq. (5) corresponds to the following mass action reaction:

$$Sor + Cont = SorCont$$
 (6)

$$K_{d}^{w} = \frac{[SorCont]}{[Sor][Cont]} \qquad [SorCont] = K_{d}^{w}[Sor][Cont] \qquad (7)$$

where *Sor* is adsorptive surface, and *SorCont* represents the adsorbed contaminant, and [] is the concentration per unit volume of water (ML⁻³). If the amount of adsorption sites [*Sor*] is very large, [*Sor*] does not change significantly when the concentration of adsorbed species [*SorCont*] remains small. Therefore the term K_d^w [*Sor*] in Eq. (7) remains constant and the adsorbed concentration is linear function of the solution concentration.

Finally, we have

$$K_d^w = \frac{K_d \rho_b}{[Sor]} \tag{8}$$

In this example, assuming [Sor]=1E+100 [mol/l] with $K_d=5 \text{ [cm}^3/\text{g]}$ and $\rho_b=1.5 \text{ [g/cm}^3$] results in $\log K_d^w = -99.1249$.

Remarks on coupling procedures: HP 1 incorporates modules simulating (i) water flow in variably-saturated media, (ii) transport of multiple components and (iii) mixed equilibrium /kinetic geochemical reactions. In HP 1, flow and transport problems are evaluated in the HYDRUS 1D module while biogeochemical problems are considered in the PHREEQC module. Therefore many of the solute transport features in HYDRUS 1D are not used and same is true for the advection-dispersion features in PHREEQC. The numerical coupling procedure of HP 1 is based on a non-iterative sequential approach solving firstly physical flow and transport processes with HYDRUS1D and subsequently chemical process with PHREEQC. In fact, solute transport in the HYDRUS 1D module is modeled as transport of inert (nonreactive) tracers since reactions are considered in the PHREEQC module.

I. HYDRUS-1D module settings

File->Project Manager-> Projects: Button: New

New Project	×
Project	
Name:	STADS
Description:	-state flow and transport of linearly adsorbed. Con;
Directory:	D:\USSL\HYDRUS1D_4\Projects\HP1-October Browse
	OK Cancel

Main Processes

× Main Processes Heading: Steady-state flow and transport of linearly adsorbed Cont Simulate Inverse Solution ? □ <u>W</u>ater Flow □ Vapor Flow □ Snow Hydrology ☑ Solute Transport General Solute Transport Major Ion Chemistry C ΟK HP1 (PHREEQC) Heat <u>T</u>ransport Cancel Root Water Uptake Г Next.. Boot Growth <u>H</u>elp

Name: STADS

Description: Steady-state flow and transport of linearly adsorbed Cont

Button: "OK"

Note: HP 1 code starts with the HYDRUS-1D module settings and then with the PHREEQC module settings!

Heading: Steady-state flow and transport of linearly adsorbed Cont Simulate: Solute Transport and check "HP1 (PHREEQC)"

Geometry Information

Geometry Informatio	n	×
Length <u>U</u> nits Omm Ocm Om	1 Number of Soil Materials 1 Number of Layers for Mass Balances 1 Decline from Vertical Axes 100 Depth of the Soil Profile	Cancel Cancel Previous Next Help

Length Units: cm Depth of the Soil Profile: 100 cm Button: "Next"

option.

Time Information



Time Units: Days *Final Time:* 100 days *Maximum Time Step:* 0.04 Leave other values on default

Note: Since the HYDRUS-1D has self-adjusting time marching scheme, the value in the "Maximum Time Step" could be set relatively big and this will not influence on the accuracy of the HYDRUS final results. PHREEQC does not have such time marching scheme, so we recommend smaller maximum time steps to be used for the accuracy of the HP 1 final results. In general, the exact value of the maximum time step depends on the particular simulation. Note that HP 1 considers as a time marching accuracy criterion the "performance index" (the product of Peclet and Courant numbers). Therefore the value of the performance index could also be used for time calculation management. For more information refer to HP 1 User Manual, p. 36 and 37 regarding Peclet number, Courant number, and the performance index.

Print Information

Number of Printed Times: 4

Note: Don't forget to change the "Select Print Times" option! Leave other values on default.

Iteration Criteria

Note: Leave all options on default

Soil Hydraulic Models

Single Porosity Models: **check** "van Genuchten-Mualem" (usually on default) *Hysteresis:* **check** "No hysteresis" (usually on default)

Water Flow Parameters

Input the data as shown below:

	Water Flo	w Paramete	rs				X
ł	Mat	Qr	Qs	Alpha	n	Ks	1
	1	0.078	0.5	0.036	1.56		1 0.5
	<u>S</u> oil Cata	og		N <u>e</u> ur	al Network Predictio	on <u> </u>	ature Dependence
		ОК	Cano	el <u>P</u> rev	rious	<u>N</u> ext	Help

Note: In case of steady-state flow, h=0 through the profile including at the both boundaries, the "Ks" value represents the infiltrating flux.

Steady-state flow with infiltration rate of 1 cm/d is given with h=0 at the upper and lower boundaries and with Ks = 1 cm/d. Since θ s = 0.5, the pore water velocity *v* is 2 cm/d.

Water Flow Boundary Condition

Upper Boundary Condition: Constant Pressure Head Lower Boundary Condition: Constant Pressure Head

Solute Transport – General Information

Solute Transport	(here	Lange Lange	X
Time Weighting Scheme C Explicit Scheme C Innki-Nicholson Scheme Implicit Scheme Mass Units: mmol Dependence on Environmental Facto Interpretature Dependence of Trans Water Content Dependence of Transport Mode	Space Weighting Sc <u>G</u> alerkin Finite Ele Upstream Weight <u>GFE with Artificial</u> <u>Stability Criterion</u> : rs sport and Reaction Par- nsport and Reaction Par- nsport and Reaction Par-	heme ements ing FE Dispersion 2 ameters arameters	Cancel Previous Next Help
 Equilibrium Model One-site sorption model (Chemical Two-site sorption model (Chemical Two Kinetic Sites Model (Particle Two Kinetic Sites Model (Based or Dual-Porosity (Mobile-Immobile Wat Dual-Porosity Model with Two-Site Nonequilibrium Dual-Permeability Model (Physical Dual-Permeability Model with eithe and Chemical Nonequilibrium) 	Nonequilbrium) Konequilbrium) Fransport Using Attachi Filtration Theory, Chei ter) Model (Physical No Sorption in the Mobile Nonequilibrium) r Immobile Water in the	nent/Detachment, mical Nonequilibriur onequilibrium) Zone (Physical and Matrix or Kinetic Si	Chemical Nonequil n) I Chemical orption (Physical
Iteration Criteria - Only for Nonlinear P 0 Absolute Concentration 1 0 Relative Concentratin T c	roblems Tolerance Ilerance	Use Tortuosity <u>F</u> ac mber <u>o</u> f Solutes:	stor
1 <u>M</u> aximum Number of Itera	ation Pul	se <u>D</u> uration:	100

Note: When using HP 1 code, we only have to specify the "Mass Units", the "Number of Solutes" and the "Pulse Duration" options! Leave other values on default.

Mass Units: **mmol** Number of Solutes: **1** Pulse Duration: **100**

HP1 Components and Database Pathway



User needs to specify the pathway to the Database and the name of all considered components.

Database pathway: D:\USSL\HYDRUS1D_4\HP1 database\PHREEQC.dat

Component: Cont (Note: It will be shown further how to add a user-defined component).

Solute Transport - Transport Parameters

Bulk D.: **1.5 g/cm³** Disp.: **1 cm Note:** Leave other values on default

Solute Transport - Reaction Parameters

Note: Leave all values on default. When using HP 1, all optional values are considered in the PHREEQC module!

Solute Transport Boundary Conditions

Upper Boundary Condition: Concentration Flux BC

Lower Boundary Condition: Zero Gradient

Solute Concentration: **0.01** *mol/kgw* Note that the dimensions here are constrained by default to **mol/kgw** or **mol/l** resp.

HYDRUS-1D – Profile Information

Menu: Conditions-> Initial Conditions>Pressure Head: Set all points at h = 0 cm **Menu:** Conditions-> Initial Conditions>Observation Points: Insert OP`s at 25, 50 and 100 cm. Leave other options on default. Menu: File->Save Data Menu: File->Exit

Soil Profile - Summary

Button "OK"

Comment: A user-defined component can be included in the listbox by manually editing of the "Species.in" file



Note: As there is not the component as *Cont* in the presented listbox, use the following three steps procedure to enter a new component.

1. Open the STADS folder

📀 🗢 📕 « Dire	ct 🕨	STADS	 ✓ ✓ Search 		<u>×</u> 0 _
Polders Polders Infitr InfitrS	Views	Name DESCRIPT.TXT HYDRUSID.DAT	Date modified 19.5.2008 г. 16:12 ч. 19.5.2008 г. 16:21 ч.	Type Text Document DAT File	Size Size KB
InfitrS3I	Ш	PROFILE.DAT SELECTOR.IN SPECIES.IN	19.5.2008 г. 16:21 ч. 19.5.2008 г. 16:21 ч. 19.5.2008 г. 16:21 ч.	DAT File IN File IN File	14 KB 3 KB 1 KB
LSP-S1 LSP-S2 LSP-S3 LSP-W1					
BROOTUPTK	Ŧ	•	m		Þ

2. Open the "SPECIES.IN" file with Notepad, and enter the new component *Cont* as shown below:



3. Close the HYDRUS-1D window of the project STADS and reopen it.

Then the new component *Cont* will be automatically entered.

II. PHREEQC module settings

Chemical composition and chemical reactions have to be specified in a "Phreeqc.in" file. We recommend using the PHREEQC software for creating the file. The PHREEQC program is not included in the HP 1 code, so the user can download it freely from the site http://www.xs4all.nl/~appt/index.html. Use the software to make a new file and save it in the HYDRUS-1D subdirectory STADS folder as "Phreeqc.in".

🖣 Organize 👻 🏢	Views	✓ [®] Burn	, y loca			?
Folders	~	Name	Date modified	Туре	Size	Ta
 InfitrS3I-A InfitrS3I-B InfitrS3I-B LSP-S1 LSP-S2 LSP-S3 LSP-W1 Onestep ROOTUP1 	ГK	DESCRIPT.TXT HYDRUSID.DAT Phreeqc.in PROFILE.DAT SELECTOR.IN SPECIES.IN	19.5.2008 г. 16:12 ч. 19.5.2008 г. 16:26 ч. 15.5.2008 г. 18:35 ч. 19.5.2008 г. 16:21 ч. 19.5.2008 г. 16:21 ч. 19.5.2008 г. 16:27 ч.	Text Document DAT File IN File DAT File IN File IN File	1 KB 1 KB 1 KB 14 KB 3 KB 1 KB	
STADS	-	4	III			

The "Phreeqc.in" file must contain the following data:

_ O X PHREEQC for Windows - D:\USSL\HYDRUS1D_4\Projects\Direct\STADS\Phreeqc.in File Edit View Calculations Help > 🔒 | % 눱 🗋 🗙 | Ͽ Input Database Grid Chart PHREEQC Keywords SOLUTION MASTER SPECIES . Cont Cont 0.0 Cont 1.0 + CALCULATE VALUES COPY SOLUTION_SPECIES DATABASE Cont = Cont END Log_k 0.0 EQUILIBRIUM_PHASES . . EXCHANGE SOLUTION 1-101 EXCHANGE_MASTER_SPECIES units EXCHANGE_SPECIES mol/kgw GAS_PHASE Cont 1e-15 INCREMENTAL REACTIONS water 0.5 + INVERSE MODELING ISOTOPES SURFACE_MASTER_SPECIES ISOTOPE_ALPHAS Sor Sor ISOTOPE_RATIOS SURFACE SPECIES H-KNOBS E- LLNL_AQUEOUS_MODEL_PARAME Sor = Sor Log k 0.0 - MIX NAMED EXPRESSIONS Sor + Cont = SorCont . ⊕ PHASES Log k -99.125 + PITZER SURFACE 1-101 . . ■ BATES -equilibrate 1 REACTION Sor 1e100 1 1e100 REACTION_TEMPERATURE SAVE - SELECTED OUTPUT TRANSPORT SOLID_SOLUTIONS cells 101 ÷ SOLUTION_MASTER_SPECIES PRINT SOLUTION_SPECIES -reset false the SOLUTION SPBEAD - SURFACE SELECTED_OUTPUT SURFACE_MASTER_SPECIES -reset false SURFACE_SPECIES -time true TITI F -solution true Defines initial solutions -distance true . -totals Cont Е Example: -molalities SorCont SOLUTION 1-10 bH 6.05 END pe 14.8 . -units ma/l III 40:5 Modified Insert

Comment: General information about the PHREEQC work. The input for the PHREEQC is arranged by keyword data blocks. Each data block begins with a line that contains a keyword (e.g. **SOLUTION_MASTER_SPECIES**) followed by additional lines related to it. Keywords and their associated data are read from a database file (*phreeqc.dat* file) at the beginning of a run to define the elements, exchange reaction, etc. After the database file is read, data are read from the input file (*phreeqc.in* file) until the first **END** keyword is encountered, after which the specified calculations are performed. Each keyword data block may have a number of identifiers (the identifiers are words that specify options or information to the keyword blocks, e.g. "Log_k", "-distance", "-molalities", "-time", etc.) many of which are optional. The identifiers may be entered in any order. Default values for identifiers are obtained if the identifier is omitted (missing). For more information see the PHREEQC Manual, p. 63.

In this example:

The new solution species (Cont) and the surface species (Sor) are not included in phreeqc.dat, so we

need to use the PHREEQC keywords: "solution_master_species", "solution_species", "surface_master_species", and "surface_species" to define these new items.

Item	Description (Meaning)
SOLUTION MASTER SPECIES	This keyword is used to define the correspondence between element
SOLUTION_MASTER_SPECIES	names and aqueous master species.
	Element name (this is the name from the listbox), master species
	(formula for the master species, including its charge), alkalinity, gram
Cont Cont 0.0 Cont 1.0	formula weight (default value used to convert input data from mass
	units to mol units) or formula (chemical formula used to calculate
	gram formula weight), gram formula weight of element.
SOLUTION SPECIES	This keyword is used to define chemical reaction and
SOLUTION_SPECIES	activity-coefficient parameters (<i>log_k</i>) for each aqueous species.
	Association reaction for aqueous species. The defined species must be
Cont = Cont	the first species to the right of the equal sign. The association reaction
	is an identity reaction for each master species.
log_k 0.0	\log_k (note that \log_k must be 0.0 for master species, i.e. $k = 1$).
	This keyword data block is used to define the temperature and
	chemical composition of initial solution. The number (1-101) is to
SOLUTION 1-101	designate the following solution composition. (In fact, we must
	specify the solution/s for all cells of the modeled profile, in our case
	100).
unite mol/kaw	Concentration units for the simulation. The default value is mmol/kgw
units mor/kgw	(millimoles per kilogram water).
	Element list (an element name, which must correspond to the items in
	the first column in SOLUTION_MASTER_SPECIES), initial
Cont 1e-15	concentration (note that it is recommended to enter some very small
	concentration instead of zero, otherwise the PHREEQC could ignore
	Cont).
	Mass of water in the solution in kg (note that the water content
	expressed in $[L^{3}L^{-3}]$ in HYDRUS is transferred in PHREEQC in
	kilogram of water per 1000 cm ³ soil. In fact, every cell of the
-water 0.5	PHREEQC discretization always has the volume of 1000 cm^3 .
	Practically, the important thing is the ratio of the water and the entire
	node/cell volume, which has to be the same both for a node
	(HYDRUS) and for a cell (PHREEQC).
SURFACE MASTER SPECIES	This keyword data block is used to define the correspondence
	between surface binding-site names and surface master species.

Sor Sor	Surface binding-site name (name of a surface binding site), surface
	master species (formula for the surface master species).
SURFACE SPECIES	This keyword is used to define a reaction and $\log K$ for each surface
	species, including surface master species.
	Association reaction for surface species. The defined species must be
Sor = Sor	the first species to the right of the equal sign. It is an identity reaction
	for the master species.
log_k 0.0	log_k (note that log_k for a master species is 0.0).
Sor Cont = SorCont	Association reaction for the mass action Equation (6) (<i>note that as we</i>
301 + Cont = 301Cont	use surface complexation reaction, here is the place for the reaction).
log_k -99.125	log_k (note that $k = K_d^w$).
SUDEACE 1 101	This keyword is used to define the amount and composition of each
SURFACE 1-101	surface in a surface assemblage
	Number ("-equilibrate" indicates that the surface assemblage is
	defined to be in equilibrium with a given solution composition),
-equilibrate I	number (solution number with which the surface assemblage is to be
	in equilibrium).
	Surface binding-site name (name of the surface binding site), sites
	(total number of sites for this binding site, in moles),
Sor 1e100 1 1e100	specific_area_per_gram (<i>specific area of surface, in m^2/g</i>), mass
	(mass of solid for calculation of surface area, in g; surface area is
	"mass" times "specific_area_per_gram").
	This key data block is used to simulate 1D transport processes. In
	PHREEQC the flow path is divided in a number of cells 1-n for
	which SOLUTION 1-n must be defined. The flow velocity in each
TRANSPORT	cell is specified by the length of the cell divided by the time step.
	However, this option is not used in HP 1 but for spatial integration
	and connection with the transport module (HYDRUS) only the
	number of cell needs to be specified.
	Indicates the number of the cells in the profile (note that this number
-cells 101	must be equal to the number of nodes determined in the HYDRUS
	module).
	This keyword data block is used to select which results are written to
PRINT	the output file.
	Changes all print options (identifiers) listed on lines 2 through 15 to
	true or false (see PHREEOC Manual. p. 120). If false is used all data
-reset false	blocks on line 2 through line 15 will NOT be printed in the output
	file
	1110.

SELECTED OUTDUT	This keyword data block is used to produce a file that is suitable for
SELECTED_001P01	processing by spreadsheets and other data-management software.
	Change print options for all identifiers from line 6 to line 20 (if the
-reset false	statement "false" is used only the identifiers marked "true" will be
	printed (see PHREEQC Manual, p. 137)
	Prints to the selected-output file the cumulative transport time since
-time true	the beginning of the run or other defined options.
	Prints solution number used for the calculation in each line of the
-solution true	selected-output file.
-distance true	Prints to the selected-output file the X-coordinate of the cell.
	Element list ("-totals" is an identifier allows definition of a list of total
	concentrations [mol/kgw] that will be written to the selected-output
	file) element list (list of elements, element valence state, exchange
	sites or surface sites for which total concentrations will be written to
-totals Cont	the selected-output file). Elements, element valence state, exchange
	sites or surface sites must have been defined in the first column of
	SOLUTION_MASTER_SPECIES, EXCHANGE_MASTER_SPECIES, or
	SURFACE_MASTER_SPECIES input. In the example, we define the
	concentration of <i>Cont</i> in the solution phase.
	Species list ("-molalities" is an identifier allows definition of a list of
	species for which concentrations [mol/kgw] will be written to the
	selected-output file), species list (list of aqueous, exchange, or surface
-molalities SorCont	species for which concentrations will be written to the selected-output
	file). Species must have been defined by SOLUTION_SPECIES,
	EXCHANGE_SPECIES, or SURFACE_SPECIES input. In the example,
	we define the adsorbed concentration of <i>Cont</i> in the solid phase.
END	This keyword ends the data input for a simulation

Note: For more information see the PHREEQC Manual for the relevant topic.

Remark: By default, HP 1 creates two types of selected-output files: "nod_inf_chem.out" and "obs_nod_chem.out". In the first one, the concentrations in the solute (-totals) and solid (-molalities) phase through the profile according to the *Print Time* steps (defined in the HYDRUS module) are presented. In the second one, the changes of concentrations with the time are presented in the both phases according to the observation nodes (also defined in the HYDRUS module).

Go back to HYDRUS-1D GUI and execute HP1.

Organize 🔻 🏢 Views 👻 🛛) Open	🚯 Burn				
olders	~	Name	Date modified	Туре	Size	
Desktop	-	Unspecified (21)				-
🖳 Dimitar		BALANCE.OUT	4.10.2008 г. 11:30 ч.	OUT File	4 KB	
Jublic Public		DESCRIPT.TXT	19.5.2008 г. 16:12 ч.	Text Document	1 KB	
🖳 Computer	=	HYDRUS1D.DAT	4.10.2008 г. 11:29 ч.	DAT File	1 KB	
🏭 OS (C:)		I_CHECK.OUT	4.10.2008 г. 11:29 ч.	OUT File	19 KB	
Ba DATAPART1 (D:)		NOD_INF.OUT	4.10.2008 г. 11:30 ч.	OUT File	82 KB	
My Documents		nod_inf_chem.out	4.10.2008 г. 11:30 ч.	OUT File	34 KB	
120 Share		obs_nod_chem26.out	4.10.2008 г. 11:30 ч.	OUT File	165 KB	
HYDRUSID HYDRUSID HYDRUSID_4 Examples GUI20508 HPI databases		obs_nod_chem51.out	4.10.2008 г. 11:30 ч.	OUT File	165 KB	
		obs_nod_chem101.out	4.10.2008 г. 11:30 ч.	OUT File	165 KB	
		OBS_NODE.OUT	4.10.2008 г. 11:30 ч.	OUT File	359 KB	
		Phreeqc.in	4.8.2008 г. 17:24 ч.	IN File	1 KB	
		phreeqc.log	25.7.2008 г. 09:37 ч.	Text Document	0 KB	
Projects Direct HPI-October CATEX		phreeqc.out	4.10.2008 г. 11:30 ч.	OUT File	2 KB	
		PROFILE.DAT	4.10.2008 г. 11:29 ч.	DAT File	14 KB	
		PROFILE.OUT	4.10.2008 г. 11:29 ч.	OUT File	12 KB	
		RUN_INF.OUT	4.10.2008 г. 11:30 ч.	OUT File	241 KB	
DECAY		selected.out	25.7.2008 г. 09:37 ч.	OUT File	1 KB	
NITRG		SELECTOR.IN	4.10.2008 г. 11:28 ч.	IN File	3 KB	
STADS		solute1.out	4.10.2008 г. 11:30 ч.	OUT File	413 KB	
Inverse	-	SPECIES.IN	4.10.2008 г. 11:28 ч.	IN File	1 KB	

When the program finishes, open the STADS folder:

HP 1 creates specific files in which the final results are stored. Get the species results from the "nod_inf_chem.out" and "obs_nod_chem.out" files. Note that for each observation node there is a separate output file.

Results can also be received from HYDRUS 1D output files:

Post-processing

Observation Points



The graph shows the *Cont* concentration according to the time at the observation points. At the first point of the profile (at 25 cm depth) the concentration is about 10 times smaller from the infiltrating one.

Profile Information





Possible modification of the example

Steady-state transport of nonlinearly adsorbed contaminant (STADSNON)

Necessary starting information:

For this modification we assume only heterogeneous reactions of a contaminant with the sorbing surface and also that adsorption process is instantaneous and described with the Freundlich equation of nonlinear type:

$$C_a = K_d C_l^{n_F} \tag{9}$$

where C_a is the adsorbed chemical concentration [MM⁻¹], C_l is the dissolved (aqueous) chemical concentration [ML⁻³], K_d is the distribution coefficient [L³M⁻¹], and n_F is the empirical Freundlich coefficient [-] and for this modification it is equal to **0.8**.

The Eq. (9) from the viewpoint of the mass action conservation (for the needs of PHREEQC module) can be written:

$$Sor + n_F Cont = SorCont \tag{10}$$

and equilibrium constant:

$$K_d^w = \frac{[SorCont]}{[Sor][Cont]^{n_F}}$$
(11)

where all terms are similar as in the previous example.

Note that the adsorption constant K_d^w is the same as in the previous example, because in the Eq. (8) the term $[Cont]^{n_F}$ is not included.

HYDRUS-1D module settings File->Project Manager-> Projects

Project Mana	iger		X
Project Groups	Projects		
Current Project	Group		
Name:	HP1-October		
Description:	HP1 Examples October meetinng		
Directory.			
Name	Description	Date	
CATEX	Steady-state flow and Cation Exchange	07.10.08	
DEGRAD	Modeling of first-order degradation	07.10.08	
DEGRAD-H1	Modeling of first-order degradation with HYDRUS	07.10.08	
STADS	Modeling Nitrogen Transport	13 10 08	
517.85	Steady state now and transport of incluny adsorbed cone	13.10.00	
			-
			-
			-
	·		_
New	Copy Rename Delete Open	Close	

Click on "STADS" project *Button:* "Copy"

Copy Project	
Project	
Old Name:	STADS
New Name:	STADSNON
Description:	Steady-state flow and transport of nonlinearly adsorbed Cont
	OK Cancel

New Name: STADSNON Description: Steady-state flow and transport of nonlinearly adsorbed Cont Button: "OK" Button: "Open" from "Project Manager" window

Note: There is no need for any change in the HYDRUS module.

PHREEQC module settings

For entering the new Eq. 12, open with PHREEQC program the "Phreeqc.in" file in the STADSNON folder.

Change in the SURFACE_SPECIES keyword data block: (*i*) the equation Sor + Cont = SorCont with the new Sor + 0.8Cont = SorCont and (*ii*) include two new identifiers: "-no_check" and "-mole_balance SorCont" as shown below:



Note: "-no_check" since the mole balance of the reaction equation is not fulfilled due to nonlinearity of the Freundlich isotherm; "-mole_balance

Save "Phreeqc.in" file and execute HP 1:

Post-processing

Observation Points

The concentrations are zero at the observation points.

Profile Information



These graphs show the *Cont* concentration distribution through the profile at the initial plus at the printed time steps (four in the example). After 100 days the concentration into the soil is equal to zero at the 15 cm from the top of the profile. Hence, the retardation properties of a soil are bigger when the nonlinear adsorption is taken into account.

HP 1 (a coupled numerical code of the HYDRUS 1D and PHREEQC-2 programs)

EXAMPLE 2 (CATEX)

Problem: Exchanging solute transport with steady-state water flow (CATEX) **Purpose:** Understanding the role of the HYDRUS and PHREEQC modules

General Information: Transport of CaCl₂ (calcium chloride) solution under saturated steady-state water flow through a soil column of 100 cm length is calculated for 100 days. The soil has 1.5 g/cm^3 bulk density, and the saturated volumetric water content is 0.5. Water flux is 1 cm/d, and inflow concentration of CaCl₂ is 0.006 mol/kgw (0.006 mmol/cm³). Solute dispersivity is 1 cm assuming no molecular diffusion. The soil initially contains a Na-K-Cl (sodium-potassium-chloride) solution in equilibrium with the cation exchange sites. The initial concentrations are: Na 1.0E-04, K 2.0 E-05, and Cl 1.2E-04 [mol/l]. Cation exchange capacity CEC (total amount of exchange sites) is 0.73 mmol_c/kg soil.

Governing equations: In HP 1 the general solute transport equation for steady-state water flow has the form:

$$\frac{\partial C_{l,i}}{\partial t} = \frac{\partial}{\partial x} \left(D^w \frac{\partial C_{l,i}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,i}}{\partial x} + R_i$$
(1)

where $i (= 1,...N_m)$ is the aqueous species number $(N_m$ is the total number of aqueous species), $C_{l,i}$ is the total dissolved concentration of the i^{th} species $[ML^{-3}]$, $\theta\theta$ is the volumetric water content $[L^3L^{-3}]$, qis the water flux $[LT^{-1}]$ and D^w is the diffusion-dispersion coefficient (L^2T^{-1}) , R_i is the general sourse/sink term due to geochemical reactions for the i^{th} species $[ML^{-3}T^{-1}]$. In this example, four transport equations for four components (Ca, Cl, Na and K) have to be solved at the same time:

$$\frac{\partial C_{l,Ca}}{\partial t} = \frac{\partial}{\partial x} \left(D_{Ca}^{w} \frac{\partial C_{l,Ca}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,Ca}}{\partial x} + R_{Ca}$$
(2)

$$\frac{\partial C_{l,Cl}}{\partial t} = \frac{\partial}{\partial x} \left(D_{Cl}^{w} \frac{\partial C_{l,Cl}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,Cl}}{\partial x} + R_{Cl}$$
(3)

$$\frac{\partial C_{l,Na}}{\partial t} = \frac{\partial}{\partial x} \left(D_{Na}^{w} \frac{\partial C_{l,Na}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,Na}}{\partial x} + R_{Na}$$
(4)

$$\frac{\partial C_{l,K}}{\partial t} = \frac{\partial}{\partial x} \left(D_K^w \frac{\partial C_{l,K}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,K}}{\partial x} + R_K$$
(5)

where R_{Ca} , R_{Cl} , R_{Na} and R_K represent the specific sink term due to the cation exchange interactions (competative adsorption), and namely Eqs. 6 to 12:

$$0.5Ca^{2+} + Na-X \leftrightarrow 0.5Ca-X_2 + Na^{+}$$

$$\begin{bmatrix} CaX_2 \end{bmatrix}^{0.5} \begin{bmatrix} Na^{+} \end{bmatrix}$$
(6)

with equilibrium constant
$$K_{Ca/Na} = \frac{1}{\left[NaX\right]\left[Ca^{2+}\right]^{0.5}}$$
 (7)

$$0.5Ca^{2+} + K - X \leftrightarrow 0.5Ca - X_2 + K^+$$

$$[C_2 X_1]^{0.5} [K^+]$$
(8)

with equilibrium constant $K_{Ca/K} = \frac{\lfloor CaX_2 \rfloor \lfloor K \rfloor}{\lfloor KX \rfloor \lceil Ca^{2+} \rceil^{0.5}}$

$$K^{+} + Na - X \leftrightarrow K - X + Na^{+}$$
⁽¹⁰⁾

with equilibrium constant $K_{K/Na} = \frac{[KX][Na^+]}{[NaX][K^+]}$ (11)

where X⁻ denotes the exchange site, $[CaX_2]$, [NaX], and [KX] are the adsorbed concentrations, $[Ca^{2+}]$, $[Na^+]$, and $[K^+]$ are the concentrations in the solution phase.

(9)

As Eq. (11) is given with Eq. (7) divided by Eq.(9) it is not informative from a mathematical point of view. However, an additional relationship can be derived from the adsorption electrical neutrality, namely the total amount of exchangeable cations are equal to cation exchange capacity:

$$[Ca-X_2] + [Na-X] + [K-X] = CEC$$
(12)

Note that Eqs. (2) to (5) have to be solved simultaneously, because terms R_{Ca} , R_{Na} and R_K are not independent but interact each other due to the exchange process (also known as "competitive adsorption") and the term "exchange" involves replacement of one chemical for another one at the solid surface. Note also that R_{Cl} is equal to zero because Cl⁻ is a nonreactive component.

Ion exchange equation in PHREEQC: The PHREEQC program solves Eqs. (6) to (11) with the socalled *half reaction terms*:

$$Ca^{2+} + 2X^{-} \leftrightarrow Ca - X_{2}$$
(13)

with equilibrium constant
$$K_{Ca} = \frac{\left[\operatorname{Ca}X_{2}\right]}{\left[\operatorname{Ca}^{2+}\right]\left[\operatorname{X}^{-}\right]^{2}} = 6.31$$
 (14)

$$Na^{+} + X^{-} \leftrightarrow Na - X$$

$$[N_{0} \mathbf{Y}]$$
(15)

with equilibrium constant
$$K_{Na} = \frac{\lfloor \operatorname{NaX} \rfloor}{\lfloor \operatorname{Na}^+ \rfloor \lfloor \operatorname{X}^- \rfloor} = 1.00$$
 (16)

$$K^{+} + X^{-} \leftrightarrow K-X$$
(17)
with equilibrium constant $K = \frac{[KX]}{[KX]} = 5.01$
(18)

with equilibrium constant
$$K_{K} = \frac{[\mathbf{K}\mathbf{X}]}{[\mathbf{K}^{+}][\mathbf{X}^{-}]} = 5.01$$
 (18)

where $[CaX_2]$, [NaX], and [KX] are the adsorbed concentrations in *mol per kilogram water*, $[Ca^{2+}]$, $[Na^+]$, and $[K^+]$ are the concentrations in the solution phase in *mol per kilogram water*, as well as $[X^-]$ is the amount of exchange sites (quantity of exchange site) in moles. Note that all dimensions are with the assumption of water density equal to 1.

For example: dividing Eq. (14) to Eq. (16) leads to:

******±

$$\frac{\left[\operatorname{CaX}_{2}\right]^{0.5}\left[\operatorname{Na^{+}}\right]}{\left[\operatorname{NaX}\right]\left[\operatorname{Ca}^{2+}\right]^{0.5}} = \frac{K_{Ca}^{0.5}}{K_{Na}} = 2.5119$$
(19)

where the term $K_{Ca}^{0.5}/K_{Na}$ represents the equilibrium constant K_{CaNa} from Eq. (7). Note that for convergence the Eqs. (14) and (16) are written in *mol of charge* form.

Remark: The cation exchange capacity CEC is generally expressed as amount of charges per unit kg soil in "mol of charge" *per kilogram soil* [mol_c/kg soil] (or *mol_c per 100g soil*). Note that in HP 1 (i.e. in the PHREEQC module) the amount of exchange sites is given in moles per cell of the model. Taking into account that the volume of each cell is always 1000 cm³, the CEC in the PHREEQC module is express always as concentration [mol/1000 cm³] or [mol/litre]. Therefore, the user must always consider the fact that the amount of the exchange sites (exchange capacity) in one cell are in *moles per 1000 cm³* (or *litre*). Recalculating CEC from unit soil to unit volume becomes as multiplying it by the bulk density of the soil: CEC [M/M] x ρ_b [M/L³] = CEC [M/L³], thus, it could be said that the CEC dimension in HP 1 is *moles per 1000 cm³ soil*.

So, in the example CEC =0.73 [mmol_c/kg soil] and $\rho_b = 1.5$ [g/cm³], therefore CEC in M/L³ = 0.0011 [mol_c/l]. Note that in PHREEQC the amount of the exchange sites (X⁻) is considered with a valence of one.

In the database of the program (*phreeqc.dat* file) various types of thermodynamic data exist. In this example, we will simulate exchange reactions (**such as Ca+2 + 2X- = CaX2**), which are included in the "EXCHANGE SPECIES" part database. Therefore, there is no need to specify any reactions in the *phreeqc.in* file /PHREEQC module/ (for more details see PHREEQC Manual, p. 293/p. 304).

Note that the initial composition is in equilibrium with the exchange sites in the beginning of the simulation. The values of initial solution are: Na 1.0E-04, K 2.0 E-05, Ca 1.0E-10 (note that there is a need of nonzero value) and Cl 1.2E-04 all in *mol per kilogram water (or litre)*. The values of the adsorbed components are: Ca-X2 8.39E-06, Na-X 5.41E-04, and K-X 5.42E-04 all in *mol per kilogram water* and their sum represents the **X**^{*} value: 0.0011 *mol*.

The initial data must be included in the program modules as follows:

- ✓ Basic Transport parameters: geometry and time information has to be specified in the HYDRUS module,
- ✓ *Water Flow parameters:* soil hydraulic model and parameters as well as the water flow initial and boundary conditions HYDRUS module;
- ✓ Solute Transport parameters: bulk density, dispersivity and molecular diffusion coefficient in free water – in HYDRUS module, note that the diffusion coefficients for all components have to be with the same value;
- ✓ Solute Transport and Reaction parameters: all parameters have to be specified in the PHREEQC module;
- ✓ Solute Transport Initial Conditions: this information has to be specified in the PHREEQC module;
- ✓ Solute Transport Boundary Conditions: note that these values have to be specified in the HYDRUS module and the dimensions are constrained by default to mol/kgw.

HYDRUS-1D module settings

File->Project Manager-> Projects: Button: New

Rename Project	
Project	
Old Name: New Name:	CATEX CATEX
Description:	Steady-state flow and Cation Exchange
	OK Cancel

Main Processes



Heading: Steady-state flow and Cation Exchange *Simulate:* Solute Transport and check "HP1 (PHREEQC)" option.

Geometry Information



Length Units: cm Depth of the Soil Profile: 100 cm

Time Information



Time Units: days *Final Time:* 100 Initial Time Step: by default Minimum Time Step: by default Maximum Time Step: 0.04

Print Information

Number of Printed Times: 4 Button: "Select Print Times" Button: "Next"

Iteration Criteria Note: Leave all options on default

Soil Hydraulic Models

Single Porosity Models: **check** "van Genuchten-Mualem" (usually on default) *Hysteresis:* **check** "No hysteresis" (usually on default)

Water Flow Parameters

Input the data as shown below:

W	ater Flo	w Paramete	rs		Tanan I	Subgost Autor and	×
	Mat	Qr	Qs	Alpha	n	Ks	I
	1	0.078	0.5	0.036	1.56	1	0.5
	<u>S</u> oil Catal	log 🗌		▼ N <u>e</u> ur	al Network Predictio	on 🗌 🗖 Iemperature	Dependence
	[OK	Cano	el <u>P</u> rev	vious	<u>N</u> ext <u>H</u>	lelp

Solute Transport – General Information

Solute Transport		×	
Time Weighting Scheme C Explicit Scheme G Inplicit Scheme Mass Units: mmol Dependence on Environmental Fact I Imperature Dependence of Tra	Space Weighting Scheme	Cancel Previous Next Help	
Nonequilibrium Solute Transport Moc Equilibrium Model Dare-site sorption model (Chemica Two-site sorption model (Chemica Two Kinetic Sites Model (Particle Two Kinetic Sites Model (Particle Two Kinetic Sites Model (Based o Dual-Porosity (Mobile-Immobile W Dual-Porosity Model with Two-Site Nonequilibrium) Dual-Permeability Model (Physica Dual-Permeability Model (Physica Dual-Permeability Model with ethe and Chemical Nonequilibrium)	els Nonequilbrium) Transport Using Attachment/Detachme n Filtration Theory, Chemical Nonequilbr ater) Model (Physical Nonequilibrium) s Sorption in the Mobile Zone (Physical & Nonequilibrium) er Immobile Water in the Matrix or Kinetic	nt, Chemical Nonequil um) nd Chemical S'orption (Physical	
Iteration Criteria - Only for Nonlinear F 0 Absolute Concentration 0 Belative Concentratin T 1 Maximum Number of Iter	Tolerance Use Tortuosity Derance Number of Solutes: ation Bulse Duration:	actor	Mass Units: mmol Number of Solutes: 4

Note that for the specified Number of Solutes the same number of transport equations will be solved.



Note: User needs to specify the pathway to the Database and the name of all considered components.

In our case:

Database pathway: D:\USSL\HYDRUS1D_4\HP1 database\PHREEQC.dat

Specify components: Cl (*chlorine*), Ca (*calcium*), Na (*sodium*), and K (*potassium*) Note that all elements are presented in the listbox.

Solute Transport - Transport Parameters

Bulk D.: **1.5 g/cm³**

Disp.: **1 cm**

Difus. W. /diffusion coefficient in free water/: $0 \text{ cm}^2/d$. Note that the diffusion coefficients for all components must have the same value /zero or different/, for more details see the HP 1 Manual, p. 15. Leave other values on default

Solute Transport - Reaction Parameters

Note: Leave all values on default. When using HP 1, all optional values are considered in the PHREEQC module!

Solute Transport Boundary Conditions



Upper Boundary Condition: Concentration Flux BC with concentrations: Cl 0.0012, Ca 0.0006, Na 0, K 0 [mol/kgw]. Lower Boundary Condition: Zero Gradient

HYDRUS-1D – Profile Information

Initial Conditions>Pressure Head: Set all points at h = 0 cm

Menu: Conditions-> Initial Conditions>Observation Points: Insert one point at the middle of profile (z= -50).

Leave other options on default.

Note that even though we have Initial conditions of the concentrations (the Na-K-Cl solution), we must define them in the PHREEQC module and not here!

Menu: File->Save Data Menu: File->Exit

Soil Profile - Summary Button "OK"

PHREEQC module settings

Use the PHREEQC software to make a new file and save it in the HYDRUS-1D subdirectory CATEX folder as "Phreeqc.in".



The "Phreeqc.in" file must contain the following data:

In this example:

Item	Description (Meaning)
TITLE Example 2. Transport and	This keyword data block is used to include a comment for a simulation in
cation exchange	the output file.
SOLUTION 1-101	This keyword data block is used to define the temperature and chemical composition of initial solution. The number (1-101) is to designate the following solution composition. (<i>in fact, we must specify the solution/s for all cells of the modeled profile, in our case 100</i>). The example assumes that the same solution is initially associated with each node, but this is not necessary.
Units mmol/kgw	Concentration units for the simulation. The default value is mmol/kgw (<i>millimoles per kilogram water</i>).
pH 7.0 charge	Indicates pH is entered on this line, pH value, charge (indicates that pH is to be adjusted to achieve charge balance, note if charge is specified for pH, it may not be specified for any other element).
water 0.5	Mass of water in the solution in kg (<i>note that</i> the water content expressed in $[L^3L^3]$ in HYDRUS is transferred in PHREEQC in kilogram of water per 1000 cm ³ soil.
Na 0.1	Element list (an element name), initial concentration.
K 0.02	Element list (an element name), initial concentration.
Ca 0.0000001	Element list (an element name), initial concentration.
Cl 0.12	Element list (an element name), initial concentration.
EXCHANGE 1-101	This keyword data block is used to define the amount and composition of

	an assemblage of exchangers. 1-101 is the positive number to designate
	the following exchange assemblage and its composition. In our case we define the same exchanger for all nodes, namely exchange site \mathbf{X} .
	Exchange site (only the name of the exchange site needs to be entered),
X 0.0011	amount (quantity of exchange site, in moles). Note that the dimension is
X 0.0011	by default always in moles . This means that every cell possesses 0.0011
	mol of the exchanger (<i>see the Remark</i> ¹).
	"-equilibrate" indicates that the exchange assemblage is defined to be in
-equilibrate 1	equilibrium with a given solution composition), number (solution number
	with which the surface assemblage is to be in equilibrium).
	This key data block is used to simulate 1D transport processes. However,
TRANSPORT	this option is not used in HP 1 but for spatial integration (integration of
	the profile) and connection with the transport module (HYDRUS) only the
	number of cell needs to be specified.
-cells 101	Indicates the number of the cells in the profile (note that this number must
	be equal to the number of nodes determined in the HYDRUS module).
PRINT	This keyword data block is used to select which results are written to the
	output file.
	Changes all print options listed on lines 2 through 15 to true or false (see
-reset false	PHREEQC Manual, p. 120). If false is used all data blocks on line 2
	through line 15 will NOT be printed in the output file.
	I his keyword data block is used to produce a file that is suitable for
SELECTED_OUTPUT	processing by spreadsneets and other data-management software. The
	the identifiers of SELECTED, OUTDUT
	"file" (identifier allows definition of the name of the file where the
	selected initial information (results) will be written) file name (file name
	where selected results will be written). Note: the file name may have
-file PHREEQC.hse	extensions "* hse" "* out" or "* sel" In the example the initial aqueous
	concentrations (Cl^{-} Ca^{2+} Na^{+} and K^{+}) and the initial adsorbed
	concentrations (CaX2, NaX, and KX) are printed.
	Change print options for all identifiers from line 6 to line 20 (if the
-reset false	statement "false" is used only the identifiers marked "true" will be printed
	(see PHREEQC Manual, p. 137)
time true	Prints to the selected-output file the cumulative transport time since the
-time true	beginning of the run or other defined options.
-distance true	Prints to the selected-output file the X-coordinate of the cell.
	Element list ("-totals" is an identifier allows definition of a list of total
	concentrations that will be written to the selected-output file) element list
	(list of elements, element valence state, exchange sites or surface sites for
	which total concentrations will be written to the selected-output file in
-totals Cl Ca Na K	mol/kgw after each calculation). Elements, element valence state,
	exchange sites or surface sites must have been defined in the first column
	of SOLUTION_MASTER_SPECIES, EXCHANGE_MASTER_SPECIES, or
	SURFACE_MASTER_SPECIES input. In the example, we define the
	concentration of Cl, Ca ⁺ , Na ⁺ , and K ⁺ in the solution phase. Note that the
	four components exist in the PHREEQC data base.
	species list (-molannes is an identifier allows definition of a list of
	species for which concentrations [mol/kgw] will be written to the
	species for which concentrations will be written to the selected output
-molalities CIX CaX2 NaX KV	file) Species must have been defined by SOLUTION SPECIES
	EXCHANGE SPECIES or SURFACE SPECIES input In the example we
	define the adsorbed concentration of $Cl^- Ca^{2+} Na^+$ and K^+ in the solid
	phase. Note that the four exchange species exist in the PHREEOC data
	base.
END	This keyword ends the data input for a simulation.

Note: For more information see the PHREEQC Manual for the relevant topic.
Remark¹: The number of exchange sites at each node is 0.0011 mol, and the initial composition of the exchanger is calculated such that it is in equilibrium with solution 1, *i.e.* cations Ca^{2+} , Na^+ , and K^+ are at all times in equilibrium with the exchanger. In the example, the initial exchange composition is calculated assuming that the composition of solution 1 is fixed; the composition of solution one is not changed when calculating the initial exchange-composition

Go back to HYDRUS-1D GUI and execute HP1.

HP 1 creates specific files in which the final results are stored. Get the species results from the "nod_inf_chem.out" and "obs_nod_chem.out" files. The first one presents the concentrations in the solute and solid phases through the profile according to the *Print Time* steps. The second one presents the changes of concentrations with the time in the both phases according to the observation nodes.

Results can also be received from HYDRUS 1D output files:

Post-processing



r obt processing



Chloride is a conservative solute and arrives in the effluent at about 20 d (*a breakthrough time*). The sodium (constant *K* with the exchange sites \mathbf{X}^{*} equal to 1, $log_K = 0.0$, resp.) initially presents in the column exchanges with the incoming calcium (constant *K* with the exchange sites \mathbf{X}^{*} equal to 6.3, $log_K = 0.8$, resp.) and it is eluted as long as the exchanger contains sodium. Because potassium (constant *K* with the exchanger \mathbf{X} equal to 5.0, $log_K = 0.7$, resp.) exchanges with calcium more strongly than sodium (larger *log K* in the exchange reaction), potassium released after sodium. The peak of the potassium concentration (0.0012 mmol/cm³) is due to the initially well absorbed K⁺ cations on the exchange sites. Finally, when all of potassium has been released (the exchange sites are filled up with the Ca²⁺ cations) and the concentration of calcium increases to a steady-state value equal to the concentration of the applied solution.

Profile Information



The Cl⁻ concentration in the solute phase through the profile at the initial time (the black graph) and at the printed time steps.

Profile Information: Concentration - 3

Profile Information: Concentration - 3

0.0005

0 0010

Next

Conc [mmol/cm3]

Previous (

through the profile at the initial time (the

black graph) and at the printed time steps.



The Ca²⁺ concentration in the solute phase through the profile at the initial time (zero value) and at the printed time steps.



The K^+ concentration in the solute phase through the profile at the initial time (the black graph) and at the printed time steps.

Note that the same process can be simulated with the UNSATCHEM code.

0 0015

Close

Profile Information Basic Profile Information

Depth

Horizontal Variable:

0

-20

-40

-80

-100

<u>D</u>efault

0.0000

Print

[c]

Depth -60

Vertical Variable:

HP 1 (a coupled numerical code of the HYDRUS 1D and PHREEQC-2 programs)

EXAMPLE 3 (DEGRAD)

Problem: Transport of linearly adsorbed component with first-order chain degradation under steady state water flow condition (DEGRAD)

Purpose: Understanding the role of the HYDRUS and PHREEQC modules in modeling first-order degradation process

General Information: Transport of the component *Conta* with first-order decay chain through a soil column of 100 cm length for a period of 100 days is simulated. The soil has 1.5 g/cm³ bulk density, and the saturated volumetric water content is 0.5. Water flux is 1 cm/d and inflow concentration of *Conat* is 0.01 mol/1 (0.01 mmol/cm³). Solute dispersivity is 1 cm neglecting molecular diffusion. *Conta* is degraded to *Contb* with first-order decay constant value of 0.02 d⁻¹. The daughter product *Contb* also decays into a new species *Contc* with first-order decay constant of 0.015 d⁻¹. Finally, *Contc* decays with first-order decay constant of 0.01 d⁻¹ as well. Those three components are linearly adsorbed with distribution coefficients K_d of 5.0 for *Conta*, 2.5 for *Contb*, and 0.75 [cm³/g] for *Contc* (Fig. 1).

Governing equations: In HP 1 the general equation describing the solute transport with various chemical reactions has the form:

$$\frac{\partial C_{l,i}}{\partial t} = \frac{\partial}{\partial x} \left(D^w \frac{\partial C_{l,i}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,i}}{\partial x} + R_i$$
(1)

where $i (= 1,...N_m)$ is the aqueous species number $(N_m$ is the total number of aqueous species), $C_{l,i}$ is the total dissolved concentration of the i^{th} species [ML⁻³], $\theta\theta$ is the volumetric water content [L³L⁻³], qis the flux [LT⁻¹] and D^w is the diffusion-dispersion coefficient (L²T⁻¹), R_i is the general source/sink term due to geochemical reactions for the i^{th} species [ML⁻³T⁻¹].

In this example, the term R_i considers two type of reactions: adsorption and first-order decay (degradation) process (Fig. 1):

$$R_{i}^{'} = -\rho_{b} \frac{\partial C_{a,i}}{\partial t}$$
⁽²⁾

and

$$R_i^{"} = -\mu C_i \tag{3}$$

where C_a is the adsorbed concentration [MM⁻¹], ρ_b is the bulk density [ML⁻³], μ is the first-order degradation constant with dimension of reciprocal time [T-¹], C_i is the total concentration of the *i*th species [ML⁻³].

Taking into account that (neglecting the gas phase)

$$C_i = \theta C_{l,i} + \rho_b C_{a,i} \tag{4}$$

equation (3) can be re-written as:

$$R_i^{"} = -\left(\mu_w \theta C_{l,i} + \mu_s \rho_b C_{a,i}\right) \tag{5}$$

where μ_w and μ_s are the first-order degradation constants for the component (species) in the liquid and solid phases, respectively.

We assume that adsorption process is instantaneous and described with the linear Freundlich equation:

$$C_a = K_d C_l \tag{6}$$

where K_d is the distribution coefficient [L³M⁻¹].



Fig. 1. The processes scheme for first-order decay chain of linearly adsorbed conponents *Conta, Contb and Contc.*

Transport equations for each component are described with:

$$\frac{\partial C_{l,Conta}}{\partial t} = \frac{\partial}{\partial x} \left(D_{Conta}^{w} \frac{\partial C_{l,Conta}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,Conta}}{\partial x} - \rho_{b} K_{d,1} \frac{\partial C_{l,Conta}}{\partial t} - \mu_{w,1} \theta C_{l,Conta} - \mu_{s,1} \rho_{b} K_{d,1} C_{l,Conta} \right)$$
(7)

$$\frac{\partial C_{l,Contb}}{\partial t} = \frac{\partial}{\partial x} \left(D_{Contb}^{w} \frac{\partial C_{l,Contb}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,Contb}}{\partial x} - \rho_{b} K_{d,2} \frac{\partial C_{l,Contb}}{\partial t} + \mu_{w,1} \theta C_{l,Conta} + \mu_{s,1} \rho_{b} K_{d,1} C_{l,Conta} - \mu_{w,2} \theta C_{l,Contb} - \mu_{s,2} \rho_{b} K_{d,2} C_{l,Contb} \right)$$
(8)

$$\frac{\partial C_{l,Contc}}{\partial t} = \frac{\partial}{\partial x} \left(D_{Contc}^{w} \frac{\partial C_{l,Contc}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,Contc}}{\partial x} - \rho_{b} K_{d,3} \frac{\partial C_{l,Contc}}{\partial t} + \mu_{w,2} \theta C_{l,Contb} + \mu_{s,2} \rho_{b} K_{d,2} C_{l,Contb} - \mu_{w,3} \theta C_{l,Contc} - \mu_{s,3} \rho_{b} K_{d,3} C_{l,Contc}$$
(9)

The linear adsorption process and its simulation in HP1 is described in details in Example 1, thus here we will explain only the first-order decay process. In PHREEQC the first-order decay is modeled with kinetics reactions using the keywords **RATES** and **KINETICS**. In the **RATES** keyword data block the kinetic reaction is defined by using short BASIC language program. The **KINETICS** data block defines the produced elements and the exact parameter values of the kinetic reaction (for more details see the PHREEQC Manual, p. 106/p. 124).

Following parameter values are used in this example: $\rho_b = 1.5 \text{ [g/cm}^3\text{]}$, $K_{d,1} = 5.0 \text{ [cm}^3/\text{g]}$, $K_{d,2} = 2.5 \text{ [cm}^3/\text{g]}$, $K_{d,3} = 0.75 \text{ [cm}^3/\text{g]}$, $[Sor]_{\text{Total}} = 1\text{E} + 100 \text{ [mol/l]}$, and resp. $\log K_{d,1}^w = -99.1249$, $\log K_{d,2}^w = -99.4259$, $\log K_{d,3}^w = -99.9488$, and decay constants are same both in the liquid and solid phases, $\mu_{w,1} = \mu_{s,1} = 0.02/d$, $\mu_{w,2} = \mu_{s,2} = 0.015/d$ and $\mu_{w,3} = \mu_{s,3} = 0.01/d$.

I. HYDRUS-1D module settings

File->Project Manager-> Projects: Button: New

New Project	
Project	
Name:	DEGRAD
Description:	Modeling of first-order degradation
Directory:	D:\USSL\HYDRUS1D_4\Projects\HP1-October
	OK Cancel

Name: DEGRAD

Description: Modeling of first-order decay *Button:* "OK"

Note: HP 1 code starts with the HYDRUS-1D module settings and then with the PHREEQC module settings!

Main Processes

Main Processes	×
Heaging: Modeling of first-order degradation	
Simulate └────────────────────────────────────	Inverse Solution ?
<u>Major Ion Chemistry</u> HP1 (PHREEQC)	ОК
Heat <u>T</u> ransport	Cancel
Boot Water Uptake Boot Growth	<u>N</u> ext
	Help

Heading: Modeling of first-order degradation
Simulate: Solute Transport and check "HP1 (PHREEQC)"
option.
Button: "Next"

Geometry Information

Length Units 1 Number of Soil Materials OK C mm 1 Number of Layers for Mass Balances Cancel C m 1 Decline from Vertical Axes Previous	Geometry Informat	ion	X
Image:	C mm C cm C m	1 Number of Soil Materials 1 Number of Layers for Mass Balances 1 Decline from Vertical Axes 100 Depth of the Soil Profile	Cancel Cancel Previous Next Help

Length Units: cm Depth of the Soil Profile: 100 cm Button: "Next"

Time Information



Time Units: Days *Final Time:* 100 days *Maximum Time Step:* 0.04 Leave other values on default

Print Information

Number of Printed Times: 4

Iteration Criteria

Leave all options by default

Soil Hydraulic Models

Single Porosity Models: **check** "van Genuchten-Mualem" (usually by default) *Hysteresis:* **check** "No hysteresis" (usually by default)

Water Flow Parameters

Input the data as shown:

Water Fl	ow Paramete	rs				×
Mat	Qr	Qs	Alpha	n	Ks	1
1	0.078	0.5	0.036	1.56		1 0.5
Soil Catalog Neural Network Prediction I remperature Dependence						
	OK	Cano	el <u>P</u> rev	ious	<u>N</u> ext	<u>H</u> elp

Water Flow Boundary Condition

Upper Boundary Condition: Constant Pressure Head Lower Boundary Condition: Constant Pressure Head

	Solute	Transport –	General	Information
--	--------	-------------	---------	-------------

Solute Transport			×
Time Weighting Scheme C. Explicit Scheme ©Irank-Nicholson Scheme OImplicit Scheme Mass Units: Implicit Scheme Dependence on Environmental Fact Iemperature Dependence of Train Water Content Dependence of Train Water Solute Transport Model One-site sorption model (Chemica Two-site sorption model (Chemica Two Kinetic Sites Model (Particle C Two Kinetic Sites Model (Based) C Due Dependence Sites Model (Based)	Space Weightin Galerkin Fini Upstream W GFE with <u>Arti</u> <u>stability</u> Criterion tors msport and Reaction ransport and Reaction ransport and Reaction al Nonequilbrium) al Nonequilbrium) Transport Using At on Filtration Theory,	g Scheme te Elements eighting FE ficial Dispersion 2 Parameters on Parameters on Parameters	Chemical Nonequil
C Dual-Porosity (Mobile-Immobile Water) Model (Physical Nonequilibrium) Dual-Porosity Model with Two-Site Sorption in the Mobile Zone (Physical and Chemical Nonequilibrium) Dual-Permeability Model (Physical Nonequilibrium) Dual-Permeability Model with either Immobile Water in the Matrix or Kinetic Sorption (Physical and Chemical Nonequilibrium)			
Iteration Criteria - Only for Nonlinear Problems Image: Concentration Tolerance 0 Absolute Concentration Tolerance 0 Belative Concentration Tolerance		3	
<u>Maximum Number of Ite</u>	ration	Pulse <u>D</u> uration:	100

Mass Units: mmol

Number of Solutes: **3** Pulse Duration: **100**

HP1 Components and Database Pathway

HP1 Components and Database Pathway					
Database Pathway: D:\USSL\HYDRUS1D_4\HP1 Databases\PHREEQC.DAT Browse					
1 2 3	Component Conta Contb Contc	Presets 	Warning: The PHREEQC.It chemical composition and needs to be written using P copied into the HYDRU The default PHREEQC.tmp file can be created using the command below.	V file specifying the chemical reactions HREEQC.GUI and S project folder.	

User needs to specify the pathway to the Database and the name of all considered components.

Database pathway: D:\USSL\HYDRUS1D_4\HP1 database\PHREEQC.dat

Component: *Conta, Contb, Contc* (**Note:** If the number of new components are more than one they can be directly added to the listbox).

Solute Transport - Transport Parameters

Bulk D.: **1.5 g/cm³** Disp.: **1 cm** Difus. W. /diffusion coefficient in free water/: **0 cm²/d Note:** Leave other values by default

Solute Transport - Reaction Parameters

Note: Leave all values on default. When using HP 1, all optional values are considered in the PHREEQC module!

Solute Transport Boundary Conditions

Upper Boundary Condition: Concentration Flux BC *Lower Boundary Condition:* Zero Gradient *Solute Concentration:* **0.01 mol/kgw (mmol/cm³). Note that** the value must be in mol per kg water.

HYDRUS-1D – **Profile Information**

Menu: Conditions-> Initial Conditions>Pressure Head: Set all points at h = 0 cm **Menu**: Conditions-> Initial Conditions>Observation Points: Insert OP`s at 25, 50 and 100 cm. Leave other options by default.

Menu: File->Save Data Menu: File->Exit

Soil Profile - Summary

Button "OK"

II. PHREEQC module settings

Chemical composition and chemical reactions have to be specified in a "Phreeqc.in" file. We recommend using the PHREEQC software for creating the file. The PHREEQC program is not included in the HP 1 code, so the user can download it freely from the site http://www.xs4all.nl/~appt/index.html. Use the software to make a new file and save it in the HYDRUS-1D subdirectory DECAY folder as "Phreeqc.in".

The "Phreeqc.in" file must contain the following data:

File Edit View Calculations Help Imput Database Grid Chart SOLUTION_MASTER_SPECIES Conta Conta 0.0 Conta 1.0 Contb Contb 0.0 Contb 1.0
Imput Database Gind Chart SOLUTION_MASTER_SPECIES Conta Conta Contb Contb
Imput Database Grid Chart SOLUTION_MASTER_SPECIES Conta Conta 0.0 Conta 1.0 Contb Contb 0.0 Contb 1.0
SOLUTION MASTER SPECIES Conta Conta 0.0 Conta 1.0 Contb Contb 0.0 Contb 1.0
Conta Conta 0.0 Conta 1.0
Contb Contb 0.0 Contb 1.0
Contc Contc 0.0 Contc 1.0
- DATABASE
SOLUTION SPECIES
Conta = Conta
log k 0
EXCHANGE_SPECIES
Contb = Contb
Contc = Contc SUTOPE AL PHAS
SOLUTION 1-101
-units mol/kgw ELUL_AQUEOUS_MODEL_PARAMETERS
Conta 1E-15
Contb 1E-15 Phases
Contc 1E-15
-water 0.5
BATES BATES
SURFACE_MASTER_SPECIES — HEALIUN_LEMPERATURE
SUPERCE SPECTES
Sorr = Sorr
log k 0
Sor + Conta = SorConta - SorConta
SURFACE_SPECIES
Sor + Contb = SorContb
log_k -99.426
Sor + Contc = SorContc Brucker
log_k -99.949
Surface 1-101
Pequilibrate 1 Defines the rate expression for kinetic
Sor lelou 1 lelou reactions in BASIC statements.
PATTER
Contadegradation Example:
-start HAIES
+ m
/ // Incert

and



and

PHREEQC for Windows - D:\USSL\HYDRUS1D_4\Projects\Direct\DECAY\PHREEQC.IN	
<u>File Edit View Calculations H</u> elp	
🗋 📂 🔚 🐁 🖻 🛍 🗙 🌍	
Input Database Grid Chart	
10 rem parm(1) first-order degradation coefficient (d-1)	PHREEQC Keywords
20 rate=parm(1)*tot("water")*mol("SorContc")	ADVECTION
30 moles=-rate*time	CALCULATE_VALUES
40 save moles	
-end	- END
	E EQUILIBRIUM PHASES
KINETICS 1-101	EXCHANGE
Contadegradation	EXCHANGE_MASTER_SPECIES
-formula Conta 1.0 Contb -1.0	EXCHANGE_SPECIES
-parms 0.02	GAS_PHASE INCREMENTAL REACTIONS
SorContadegradation	
-tormula SorConta 1.0 Contb -1.0	ISOTOPE_ALPHAS
-parms 0.02	ISOTOPE_RATIOS
	KINETICS
Contbdegradation	
-Iormala Conto I.U Conte -1.U	MIX
-parms 0.015	NAMED EXPRESSIONS
PorConthdegradation	
-formula SorConth 1 0 Contr -1 0	I PITZER
-parms 0 015	E PRINT
F	H- HAIES REACTION
Contcdegradation	- BEACTION TEMPEBATURE
-formula Contc 1.0	- SAVE
-parms 0.01	E SELECTED_OUTPUT
	SOLID_SOLUTIONS
SorContcdegradation	E SULUTION MASTER SPECIES
-formula SorContc 1.0	
-parms 0.01	SOLUTION_SPREAD
TRANSPORT	
-cells 101	E SURFACE_SPECIES
DDTM	TRANSPORT
-reset false	USE
TCSCC TAISE	USER_GRAPH
	USER_PRINT
-file PHREFOC.bse	USER_PUNCH DUREFOR PACIF states
-reset false	
-time true	
-solution true	Specifies kinetic reactions, chemical formulas 🔺
-totals Conta Contb Contc	of reactants and reaction parameters.
-molalities SorConta SorConb SorContc	Example:
	KINETICS 1-10
END	- Calcite
< III >	-formula CaCO3 1.0 🗸
132:4 Insert	

In this example:

The new solution species (*Conta, Contb* and *Contc*) and the surface species (*Sor*) are not included in *phreeqc.dat*, so we need to use the PHREEQC keywords: "solution_master_species", "solution_species", "surface_master_species", and "surface_species" to define these new items.

Item	Description (Meaning)
SOLUTION_MASTER_SPECIES	This keyword is used to define the correspondence between element names and aqueous master species.
Conta Conta 0.0 Conta 1.0 Contb Contb 0.0 Contb 1.0 Contc Contc 0.0 Contc 1.0	Element name (<i>this is the name from the listbox</i>), master species (<i>formula for the master species, including its charge</i>), alkalinity, gram formula weight (<i>default value used to convert input data</i> <i>from mass units to mol units</i>) <i>or</i> formula (chemical formula used

	to calculate gram formula weight), gram formula weight of
	element.
SOLUTION SPECIES	This keyword is used to define chemical reaction and
SOLUTION_SPECIES	activity-coefficient parameters (k) for each aqueous species.
	Association reaction for aqueous species. The defined species
Conto - Conto	must be the first species to the right of the equal sign. The
Conta – Conta	association reaction is an identity reaction for each master
	species.
log_k 0.0	log k (note that log k must be 0.0 for master species, i.e. $k = 1$).
	Association reaction for aqueous species. The defined species
Conth - Conth	must be the first species to the right of the equal sign. The
	association reaction is an identity reaction for each master
	species.
log_k 0.0	log k (note that log k must be 0.0 for master species, i.e. $k = 1$).
	Association reaction for aqueous species. The defined species
Contc = Contc	must be the first species to the right of the equal sign. The
cone – cone	association reaction is an identity reaction for each master
	species.
log_k 0.0	log k (note that log k must be 0.0 for master species, i.e. $k = 1$).
	This keyword data block is used to define the temperature and
	chemical composition of initial solution. The number (1-101) is
SOLUTION 1-101	to designate the following solution composition. (In fact, we
	must specify the solution/s for all cells of the modeled profile, in
	our case 100).
Units mol/kgw	Concentration units for the simulation. The default value is
	mmol/kgw (millimoles per kilogram water).
	Element list (an element name, which must correspond to the
Conta 1e-15	items in the first column in SOLUTION_MASTER_SPECIES),
Contb 1e-15	initial concentration (note that it is recommended to enter some
Contc 1e-15	very small concentration instead of zero, otherwise the
	PHREEQC could ignore the component).
	Mass of water in the solution in kg (<i>note that the water content</i>
	expressed in $[L^{2}L^{2}]$ in HYDRUS is transferred in PHREEQC in
	kilogram of water per 1000 cm ³ soil. In fact, every cell of the
-water 0.5	PHREEQC discretization always has the volume of 1000 cm ³ .
	Practically, the important thing is the ratio of the water and the
	entire node/cell volume, which has to be the same both for a
	node (HYDRUS) and for a cell (PHREEQC).

SUDEACE MASTED SDECIES	This keyword data block is used to define the correspondence
SURFACE_MASTER_SPECIES	between surface binding-site names and surface master species.
Son Son	Surface binding-site name (name of a surface binding site),
501 501	surface master species (formula for the surface master species).
	This keyword is used to define a reaction and $\log K$ for each
SUNFACE_SFECIES	surface species, including surface master species.
	Association reaction for surface species. The defined species
Sor = Sor	must be the first species to the right of the equal sign. It is an
	identity reaction for the master species.
log_k 0.0	log k (note that $log k$ for a master species is 0.0).
	Association reaction for the mass action equation for the linear
Sor - Conto - SorConto	adsorption (note that as we use surface complexation reaction,
Sor + Conta – SorConta	here is the place for the reaction). Note that the dimension of
	SorConta is mol/kgw.
log_k -99.125	log k (note that $k = K_{d1}^{W}$). $K_{d1}^{W} = K_{d,1} * \rho_b / [Sor]$
Sor - Conth - SorConth	Association reaction for the mass action equation for the linear
Sor + Conto = SorConto	adsorption process.
log_k -99.426	log k (note that $k = K_{d2}^{w}$). $K_{d2}^{w} = K_{d,2*}\rho_b/[Sor]$
	Association reaction for the mass action equation for the linear
Sor + Contc = SorContc	adsorption process.
log_k -99.949	log k (note that $k = K_{d3}^{w}$). $K_{d3}^{w} = K_{d,3*}\rho_b/[Sor]$
	This keyword is used to define the amount and composition of
SURFACE I-101	each surface in a surface assemblage
	Number ("-equilibrate" indicates that the surface assemblage is
	defined to be in equilibrium with a given solution composition),
-equilibrate I	number (solution number with which the surface assemblage is
	to be in equilibrium)
	Surface binding-site name (name of the surface binding site),
	sites (total number of sites for this binding site, in moles),
Sor 1e100 1 1e100	specific_area_per_gram (<i>specific area of surface, in m^2/g</i>), mass
	(mass of solid for calculation of surface area, in g; surface area
	is "mass" times "specific_area_per_gram").
	This keyword data block is used to define mathematical rate
	expressions for kinetic reactions. Note that general rate
RATES	formulas are defined in the RATES data block and specific
	parameters for transport kinetics are defined in the KINETICS
	data block.
Contadegradation	name of rate expression - alphanumeric character string that

	identifies the rote expression
	identifier marks the beginning of a BASIC program by which
-start	the moles of reaction for a time subinterval are calculated.
	BASIC language program is written from lines 10 to 40.
10 rem parm(1) first-order degradation	numbered BASIC statement – rem is only a comment (without
coefficient (d-1)	effect on the calculations) indicating the meaning of the first
	parameter, which is first-order degradation coefficient
	numbered BASIC statement - rate defines the rate of
20 rate-narm(1)*tot("water")*mol("Conta")	degradation in the liquid phase, <i>parm</i> (1) is the first-order rate
20 rate-parm(1) tot (water) mon conta)	constant, tot("water") and mol("Conta") are the amounts of
	water and solute concentration in the cell.
	numbered BASIC statement - moles integrates the rate over the
	time subinterval with the special variable time. Note that the
	negative sign results in a negative amount of moles saved in the
30 moles=-rate* <i>time</i>	last statement (line 40). In general, a negative sign means that
	elements will be removed from the solution (i.e. precipitation,
	degradation, or decay).
40	numbered BASIC statement – save the moles of reaction during
40 save moles	the time interval are saved
	Identifier marks the end of the BASIC program by which the
	number of moles of a reaction for a time subinterval is
-end	calculated. Note the hyphen is required to avoid a conflict with
	the keyword END.
	name of rate expression - alphanumeric character string that
SorContadegradation	identifies the rate expression. In this case, it represents the
	degradation of the solid (adsorbed) phase of the component.
	identifier marks the beginning of a BASIC program by which
-start	the moles of reaction for a time subinterval are calculated.
	BASIC language program is written from lines 10 to 40.
	numbered BASIC statement - rem is only a comment (without
10 rem parm(1) first-order degradation	effect on the calculations) indicating the meaning of the first
coefficient (d-1)	parameter, which is first-order degradation coefficient
	numbered BASIC statement - rate defines the rate of
	degradation in the solid phase, parm(1) is the first-order rate
	constant, tot("water") and mol("SorConta") are the amounts of
20 rate= <i>parm</i> (1)* <i>tot</i> ("water")* <i>mol</i> ("SorConta")	water and adsorbed concentration in the cell. Note that, as we
	defined the adsorbed concentration ("SorConta") in mol/kgw,
	this equation is the same as the equation in "Contadegradation"

	data block.
	numbered BASIC statement – moles integrates the rate over the
	time subinterval with the special variable time. Note that the
30 moles=-rate*time	negative sign results in a negative amount of moles saved in the
50 moles—rate time	last statement (line 40). In general, a negative sign means that
	elements will be removed from the solution (i.e. precipitation,
	degradation, or decay).
40 serve moles	numbered BASIC statement – save the moles of reaction during
40 save moles	the time interval are saved
	Identifier marks the end of the BASIC program by which the
	number of moles of a reaction for a time subinterval is
-end	calculated. Note the hyphen is required to avoid a conflict with
	the keyword END.
Contbdegradation	the same as for the Contadegradation data block
-start	the same as for the Contadegradation data block
10 rem parm(1) first-order degradation	
coefficient (d-1)	the same as for the Contadegradation data block
20 rate=parm(1)*tot("water")*mol("Contb")	the same as for the Contadegradation data block
30 moles=-rate* <i>time</i>	the same as for the Contadegradation data block
40 save moles	the same as for the Contadegradation data block
-end	the same as for the Contadegradation data block
SorContbdegradation	the same as for the SorContadegradation data block
-start	the same as for the SorContadegradation data block
10 rem parm(1) first-order degradation	
coefficient (d-1)	the same as for the SorContadegradation data block
20 rate=parm(1)*tot("water")*mol("SorContb")	the same as for the SorContadegradation data block
30 moles=-rate*time	the same as for the SorContadegradation data block
40 save moles	the same as for the SorContadegradation data block
-end	the same as for the SorContadegradation data block
Contcdegradation	the same as for the Contadegradation
-start	the same as for the Contadegradation
10 rem parm(1) first-order degradation	
coefficient (d-1)	the same as for the Contadegradation
20 rate=parm(1)*tot("water")*mol("Contc")	the same as for the Contadegradation
30 moles=-rate* <i>time</i>	the same as for the Contadegradation
40 save moles	the same as for the Contadegradation
-end	the same as for the Contadegradation
SorContcdegradation	the same as for the SorContadegradation data block

-start	the same as for the SorContadegradation data block
10 rem parm(1) first-order degradation coefficient (d-1)	the same as for the SorContadegradation data block
20 rate=parm(1)*tot("water")*mol("SorContc")	the same as for the SorContadegradation data block
30 moles=-rate* <i>time</i>	the same as for the SorContadegradation data block
40 save moles	the same as for the SorContadegradation data block
	This keyword data block is used to identify kinetic reactions and
	to specify reaction parameters to a specific cell. The number
KINETICS I-101	(1-101) is to designate the following set of kinetic reactions to
	the number of cells.
Contradagradation	name of rate expression. The rate name must correspond to the
Contadegradation	RATES data block
	Chemical formula or the name of the phase to be added by the
	kinetic reaction, Conta; stoichiometric coefficient 1, defines the
	mole transfer coefficient for formula per mole of reaction
	progress evaluated by the rate expression in RATES). Note that
-formula Conta 1 Contb -1.0	the user should identify which solution species appear or
	disappear. The stoichiometric coeff. "1.0" after the Conta has
	positive sign which means Conta disappears . The stoichiometric
	coeff. "-1.0" after the Contb represents the mole trasfer
	coefficient and the sign is negative which means <i>Contb</i> appears.
	list of parameters -defining parameters in the rate expression,
-parms 0.02	note that the dimension of the parameter (day ⁻¹) is defined in
	the HYDRUS Time Information window.
SorContadegradation	name of rate expression. The rate name must correspond to the
	RATES data block
	Chemical formula or the name of the phase to be added by the
	kinetic reaction, SorConta; stoichiometric coefficient 1, defines
	the mole transfer coefficient for formula per mole of reaction
	progress evaluated by the rate expression in RATES). Note that
-formula SorConta 1 Contb -1.0	the user should identify which species appear or disappear. The
	stoichiometric coeff. "1.0" after the SorConta has positive sign
	which means SorConta disappears. The stoichiometric coeff.
	"-1.0" after the <i>Contb</i> represents the mole transfer coefficient
	and the sign is negative which means <i>Contb</i> appears.
	list of parameters -defining parameters in the rate expression,
-parms 0.02	note that the dimension of the parameter (day ⁻¹) is defined in
	the HYDRUS Time Information window.

Conthelegradation	name of rate expression. The rate name must correspond to the
Contodegradation	RATES data block
	Chemical formula or the name of the phase to be added by the
	kinetic reaction, Contb; stoichiometric coefficient 1, defines the
	mole transfer coefficient for formula per mole of reaction
-formula Contb 1 Contc -1.0	progress evaluated by the rate expression in RATES). Note that
	the user should identify which solution species appear or
	disappear. The stoichiometric coeff. "-1.0" represents the mole
	transfer coefficient.
	list of parameters -defining parameters in the rate expression,
-parms 0.015	note that the dimension of the parameter (day ⁻¹) is defined in
	the HYDRUS Time Information window.
	name of rate expression. The rate name must correspond to the
SorContbdegradation	RATES data block
	Chemical formula or the name of the phase to be added by the
	kinetic reaction, SorContb; stoichiometric coefficient 1, defines
	the mole transfer coefficient for formula per mole of reaction
	progress evaluated by the rate expression in RATES). Note that
-formula SorContb 1 Contc -1.0	the user should identify which species appear or disappear. The
	stoichiometric coeff. "1.0" after the SorContb has positive sign
	which means SorContb disappears. The stoichiometric coeff.
	"-1.0" after the <i>Contc</i> represents the mole transfer coefficient
	and the sign is negative which means <i>Contc</i> appears.
	list of parameters -defining parameters in the rate expression,
-parms 0.015	note that the dimension of the parameter (day ⁻¹) is defined in
	the HYDRUS Time Information window.
Contrologradation	name of rate expression. The rate name must correspond to the
	RATES data block
	Chemical formula or the name of the phase to be added by the
formula Conte 1	kinetic reaction, Contc; stoichiometric coefficient 1, defines the
	mole transfer coefficient for formula per mole of reaction
	progress evaluated by the rate expression in RATES).
	list of parameters -defining parameters in the rate expression,
-parms 0.010	note that the dimension of the parameter (day ⁻¹) is defined in
	the HYDRUS Time Information window.
SorContedegradation	name of rate expression. The rate name must correspond to the
	RATES data block
-formula SorContc 1.0	Chemical formula or the name of the phase to be added by the

	kinetic reaction, SorContc; stoichiometric coefficient 1, defines
	the mole transfer coefficient for formula per mole of reaction
	progress evaluated by the rate expression in RATES).
	list of parameters -defining parameters in the rate expression,
-parms 0.01	note that the dimension of the parameter (day ⁻¹) is defined in
	the HYDRUS Time Information window.
	This key data block is used to simulate 1D transport processes.
	However, this option is not used in HP 1 but for spatial
TRANSPORT	integration (integration of the profile) and connection with the
	transport module (HYDRUS) only the number of cell needs to
	be specified.
	Indicates the number of the cells in the profile (note that this
-cells 101	number must be equal to the number of nodes determined in the
	HYDRUS module).
	This keyword data block is used to select which results are
PRINI	written to the output file.
	Changes all print options (identifiers) listed on lines 2 through
react false	15 to true or false (see PHREEQC Manual, p. 120). If false is
-reset faise	used all data blocks on line 2 through line 15 will NOT be
	printed in the output file.
	This keyword data block is used to produce a file* that is
SELECTED_OUTPUT	suitable for processing by spreadsheets and other
	data-management software.
	"-file" (identifier allows definition of the name of the file where
file DUDEEOC hee	the selected initial information (results) will be written), file
-THE FRIEDCLISE	name (file name where selected results will be written). Note:
	the file name may have extensions "*. <i>hse</i> ", "*. <i>out</i> ", or "*. <i>sel</i> ".
	Change print options for all identifiers from line 6 to line 20 (if
-reset false	the statement "false" is used only the identifiers marked "true"
	will be printed (see PHREEQC Manual, p. 137)
time true	Prints to the selected-output file* the cumulative transport time
-une uue	since the beginning of the run or other defined options.
solution true	Prints solution number used for the calculation in each line of
-solution true	the selected-output file.
	Element list ("-totals" is an identifier allows definition of a list
-totals Conta Conth Conte	of total concentrations [mol/kgw] that will be written to the
-totals conta conto conte	selected-output file) element list (list of elements for which total
	concentrations will be written).

			Species list ("-molalities" is an identifier allows definition of a
			list of species for which concentrations [mol/kgw] will be
-molalities	SorConta	SorContb SorContc	written to the selected-output file), species list (list of aqueous,
			exchange, or surface species for which concentrations will be
			written to the selected-output file).
	ENI)	This keyword ends the data input for a simulation

Note: For more information see the PHREEQC Manual for the relevant topic.

Go back to HYDRUS-1D GUI and execute HP1.

When the program finishes, open the DEGRAD folder:

HP 1 creates specific files in which the final results are stored. Get the species results from the "nod_inf_chem.out" and "obs_nod_chem.out" files. Note that for each observation node there is a separate output file.

Results can also be received from HYDRUS 1D output files:

Post-processing

Observation Points



These graphs show the *components* concentration according to the time at the observation point 1 (25 cm of the profile). At the end of the simulation period the second degradation daughter product has the biggest impact. Its value is almost 30% of the infiltrating concentration of *Conta*. The first daughter product (*Contb*) is only 7% from the *Conta*. Hence, only the *Contc* concentration has to be considered as the value of *Conta* (the infiltrating component) is practically zero and *Contb* (first daughter product) is very small.

Profile Information



These graphs show the *Conta* concentration distribution through the profile at the initial plus at the printed time steps (four in the example). Approximately from 15 cm of the profile, the *Conta* concentration is equal to zero.

Profile Information



These graphs show the *Contb* concentration distribution through the profile at the initial plus at the printed time steps. The maximum value of *Contb* is at 10 cm from the top of the profile and it is almost equal to the half of the infiltrating one. At the middle of the profile *Contb* concentration is zero.

Profile Information



These graphs show the *Contc* concentration distribution through the profile at the initial plus at the printed time steps. At the first quarter of the profile the concentration is at maximum $(0.0034 \text{ mmol/cm}^3)$, which is one-third from the infiltrating one.

The same problem could be simulated with HYDRUS 1D code.

HYDRUS 1D Project manager-> New project DECAY-HYD



Use the same values as in the example, change only:

Time Information

Maximum Time Step: 50

Mat	SinkSolid	1 Si	nkGas	s 1	SinkWater1	' SinkSoli	11' Si	inkGas1	•
1		0		0	0.0	2 0.02			(
•									•

Solute Transport and Reaction Parameters – Solute 1



Solute Transport and Reaction Parameters – Solute 2

	ansport and Rea	ction Paran	nete	rs - Solute 2	Hadreson Press	
Mat	SinkSolid1	SinkGa	s1	SinkWater1'	SinkSolid1'	SinkGas1'
1	0		0	0.015	0.015	(
•	-					•
	K C	ancel	P	revinus	Next	Heln

Kd: **2.5 g/cm³** *SinkWater1* `: **0.015 d⁻¹** *SinkSolid1* `: **0.015 d⁻¹**

Solute Transport and Reaction Parameters – Solute 3

 Dota		Henry	SinkW	/ater1 Si	nkSolid1	SinkG	ias1
	1		0	0.01 0.0	1		0
						_	•



Solute Transport Boundary Conditions



Bound. Cond : 0.01 mmol/cm³

Execute HYDRUS 1D

Post-processing

Observation Nodes



These graphs show the *components* concentration according to the time at the observation point 1 (25 cm of the profile). **Note that** the results are identical with the HP 1 code results.

Profile Information



These graphs show the *Conta* concentration distribution through the profile at the initial plus at the printed time steps. **Note that** the results are identical with the HP 1 code results.

Profile Information





Profile Information



These graphs show the *Contc* concentration distribution through the profile at the initial plus at the printed time steps. **Note that** the results are identical with the HP 1 code results.

HP 1 (a coupled numerical code of the HYDRUS 1D and PHREEQC-2 programs)

EXAMPLE 4 (NITROG)

Problem: Transport of linearly adsorbed organic nitrogen with first-order chain decay with cation exchange under steady-state water flow (NITROG)

Purpose: Understanding the role of the HYDRUS and PHREEQC modules due to nitrogen transport modeling

General Information: Transport of organic nitrogen fertilizer (Org-N) with steady-state water flow through a soil column of 100 cm length is simulated for 100 days. The soil has 1.5 g/cm³ bulk density, and the saturated volumetric water content is 0.5. Water flux is 1 cm/d. The soil initially contains a Na-K-Cl (sodium-potassium-chloride) solution in equilibrium with the cation exchange sites. The initial concentrations are: Na 1.0E-03, K 1.0 E-03, and Cl 2.0E-03 in mol/l. The soil has cation exchange capacity CEC of 6.7 mmol/kg soil. Solute dispersivity is 1 cm assuming no molecular diffusion.

The inflow concentration of Org-N is 0.001 mol/l (0.001 mmol/cm³). The organic nitrogen is adsorbed with distribution coefficient $K_{d,1} = 5.0 \text{ [cm}^3/\text{g]}$. Due to the *nitrification* process the organic nitrogen transforms to ammonium ion (NH₄⁺) with the first-order degradation constant value of 0.02 d⁻¹, and then to nitrate ion (NO₃⁻) with 0.015 d⁻¹. Finally, due to the *denitrification* process nitrate transforms to nitrogen gas (N₂) with the first-order constant of 0.01 d⁻¹.

Governing equations: In HP 1 the general equation describing the solute transport for steady-state water flow has the form:

$$\frac{\partial C_{l,i}}{\partial t} = \frac{\partial}{\partial x} \left(D^w \frac{\partial C_{l,i}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,i}}{\partial x} + R_i$$
(1)

In this example, the term R_i includes three types of reactions – first-order decay (degradation), adsorption, and cation exchange processes (Fig. 1):

$$\begin{array}{c|c} Org-N \xrightarrow{degradation} NH_{4} + \xrightarrow{degradation} NO_{3} - \xrightarrow{degradation} N_{2} \\ \downarrow_{K_{d,l}} & \downarrow_{N_{d}} & \downarrow_{N_{d}} & \downarrow_{N_{d}} \\ \downarrow_{K_{d,l}} & \downarrow_{degradulion} & \downarrow_{N_{d}} & \downarrow_{N_{d}} & \downarrow_{N_{d}} \\ SorOrg_N & NH4-X & \xrightarrow{SorNO_{3}} - \end{array}$$

Fig. 1. The processes scheme for first-order degradation chain of linearly adsorbed component Org-N, NH_4^+ , NO_3^- , and N_2 .

In order to simplify the model we make the following assumptions:

(i) Adsorption process of the Org-N is instantaneous and described with the Freundlich equation of linear type:

$$C_a = K_d C_l \tag{2}$$

where C_a is the adsorbed concentration [MM⁻¹], C_l is the solution concentration [ML⁻³], and K_d is the distribution coefficient [L³M⁻¹].

(ii) The ammonium ion adsorption is fully described with the cation exchange process and therefore is connected with the value of the Cation Exchange Capacity (CEC):

$$nNH_{4}^{+} + Cation-X_{n} = nNH4-X + Cation^{n+}$$
(3)
with equilibrium constant $K_{NH4/Cation} = \frac{[NH4-X]^{n} [Cation^{n+}]}{[Cation-X_{n}] [NH4^{+}]^{n}}$ (4)

where X^- represents the amount of exchange sites in $[MM^{-1}]$ or $[ML^{-3}]$, Cationⁿ⁺ represents any cation in the soil profile, [NH4-X], $[Cation-X_n]$ are the adsorbed concentrations in $[MM^{-1}]$, and $[NH4^+]$, $[Cation^{n+}]$ are the concentrations in the solution phase in $[ML^{-3}]$.

(iii) there is no adsorption of the nitrate ion to the solid phase, i.e. $K_d = 0$ (Fig. 1).

Tranport equations for each component can be discribed with:

$$\frac{\partial C_{l,Org-N}}{\partial t} = \frac{\partial}{\partial x} \left(D_{Org-N}^{w} \frac{\partial C_{l,Org-N}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,Org-N}}{\partial x} - \rho_{b} K_{d,1} \frac{\partial C_{l,Org-N}}{\partial t} - \mu_{w,1} \theta C_{l,Org-N} - \mu_{s,1} \rho_{b} K_{d,1} C_{l,Org-N}$$
(5)

$$\frac{\partial C_{l,NH_4}}{\partial t} = \frac{\partial}{\partial x} \left(D_{NH_4}^w \frac{\partial C_{l,NH_4}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,NH_4}}{\partial x} - \rho_b \frac{\partial C_{NH_4-X}}{\partial t} + \mu_{w,l} \theta C_{l,Org-N} + \mu_{s,l} \rho_b K_{d,l} C_{l,Org-N} - \mu_{w,2} \theta C_{l,NH_4} - \mu_{s,2} \rho_b C_{NH_4-X}$$
(6)

$$\frac{\partial C_{l,NO_{3}^{-}}}{\partial t} = \frac{\partial}{\partial x} \left(D_{NO_{3}^{-}}^{w} \frac{\partial C_{l,NO_{3}^{-}}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,NO_{3}^{-}}}{\partial x} + \mu_{w,2} \theta C_{l,NH_{4}} + \mu_{s,2} \rho_{b} C_{NH4-X} - \mu_{w,3} \theta C_{l,NO_{3}^{-}}$$
(7)

$$\frac{\partial C_{l,Na}}{\partial t} = \frac{\partial}{\partial x} \left(D_{Na}^{w} \frac{\partial C_{l,Na}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,Na}}{\partial x} + R_{Na}$$
(8)

$$\frac{\partial C_{l,K}}{\partial t} = \frac{\partial}{\partial x} \left(D_K^w \frac{\partial C_{l,K}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,K}}{\partial x} + R_K$$
(9)

$$\frac{\partial C_{l,Cl}}{\partial t} = \frac{\partial}{\partial x} \left(D_{Cl}^{w} \frac{\partial C_{l,Cl}}{\partial x} \right) - \frac{q}{\theta} \frac{\partial C_{l,Cl}}{\partial x} + R_{Cl}$$
(10)

where R_{Na} , R_K , and R_{Cl} , represent the specific sink terms due to the cation exchange (not considered for the chloride).

In this example, ternary cations, i.e., NH₄⁺, Na⁺, and K⁺, exchange each other and the exchange reactions can be described with following equations:

$$NH4^+ + Na-X \leftrightarrow NH4-X + Na^+$$
 (11)

with equilibrium constant
$$K_{NH4/Na} = \frac{\left[\text{NH4-X}\right]\left[\text{Na}^{+}\right]}{\left[\text{Na-X}\right]\left[\text{NH4}^{+}\right]}$$
 (12)

$$NH4^{+} + K - X \iff NH4 - X + K^{+}$$
(13)

_

with equilibrium constant
$$K_{NH4/K} = \frac{\left[\text{NH4-X}\right]\left[\text{K}^{+}\right]}{\left[\text{K-X}\right]\left[\text{NH4}^{+}\right]}$$
 (14)

$$K^+ + Na-X \leftrightarrow K-X + Na^+$$
 (15)

with equilibrium constant
$$K_{K/Na} = \frac{[KX][Na^+]}{[NaX][K^+]}$$
 (16)

where [NH4-X], [Na-X], and [K-X] are the adsorbed concentrations, [NH4⁺], [Na⁺], and [K⁺] are the concentrations in the solution phase. As shown in Example 2, an additional relationship can be based on the adsorption electrical neutrality:

$$[C_a X_2] + [N_a X] + [K X] = CEC$$
 (17)

Since this example is an assemble of reactions described in previous examples, please refer to Example 1 for the linear adsorption process, Example 2 for the cation exchange process, and Example 3 for the first-order chain degradation process.

I. HYDRUS-1D module settings

File->Project Manager-> Projects: Button: New

New Project	
Project	
Name:	NITROG
Description:	Modeling Nitrogen transport
Directory:	D:\USSL\HYDRUS1D_4\Projects\HP1-October
	OK Cancel

Name: NITROG Description: Modeling Nitrogen transport Button: "OK"

Main Processes



Geometry Information



Length Units: cm Depth of the Soil Profile: 100 cm Button: "Next"

Time Information



Time Units: Days *Final Time:* 100 days *Maximum Time Step:* 0.04 Leave other values on default

Print Information

Number of Printed Times: 4

Iteration Criteria

Leave all options by default

Soil Hydraulic Models

Single Porosity Models: check "van Genuchten-Mualem" (usually by default) Hysteresis: check "No hysteresis" (usually by default)

Water Flow Parameters

Input the data as shown:

V	Vater Flo	w Parameter	2		internal internal	Strappell' Million	×
	Mat	Qr	Qs	Alpha	n	Ks	I
	1	0.078	0.5	0.036	1.56		1 0.5
	<u>S</u> oil Catal	log		▼ Neur	al Network Predictio	n 🗌 🗆 <u>T</u> empe	rature Dependence
	(OK	Cano	el <u>P</u> rev	ious	Next	Help

Note: In case of steady-state flow, h=0 through the profile including at the both boundaries, the "Ks" value represents the infiltrating flux.

Water Flow Boundary Condition

Upper Boundary Condition: Constant Pressure Head Lower Boundary Condition: Constant Pressure Head

Solute Transport – General Information

Time Weighting Scheme	Space Weighting Scheme © <u>G</u> alerkin Finite Elements	ОК
<u>C</u> rank-Nicholson Scheme	O Upstream Weighting FE	Cancel
C Implicit Scheme	GFE with <u>A</u> rtificial Dispersion	Previous
Mass <u>U</u> nits: Immol	Stability Criterion: 2	<u>N</u> ext
Dependence on Environmental Fact <u>I</u> emperature Dependence of Tran	nsport and Reaction Parameters	Help
-	rianopole obligri kaorimone o saorimone,	Chemical Nonequil
 Two Kinetic Sites Model (Based (Dual-Porosity (Mobile-Immobile W Dual-Porosity Model with Two-Sit Nonequilibrium) Dual-Permeability Model (Physica Dual-Permeability Model with eth and Chemical Nonequilibrium) 	on Filtration Theory, Chemical Nonequilibriun /ater) Model (Physical Nonequilibrium) te Sorption in the Mobile Zone (Physical and al Nonequilibrium) ter Immobile Water in the Matrix or Kinetic So	Chemical Nonequil 1) I Chemical prption (P'hysical
C Two Kinetic Sites Model (Based (Dual-Porosity (Mobile-Immobile W Dual-Porosity Model with Two-Sit Nonequilibrium) C Dual-Permeability Model (Physica Dual-Permeability Model with eith and Chemical Nonequilibrium) Iteration Criteria - Only for Nonlinear F Absolute Concentration Belative Concentration T	on Filtration Theory, Chemical Nonequilibriun /ater) Model (Physical Nonequilibrium) te Sorption in the Mobile Zone (Physical and al Nonequilibrium) ter Immobile Water in the Matrix or Kinetic Si Problems Tolerance olerance Vumber of Solutes:	Chemical Nonequil n) I Chemical protion (Physical stor

Mass Units: **mmol** Number of Solutes: **6** Pulse Duration: **100**

HP1 Components and Database Pathway



User needs to specify the pathway to the Database and the name of all considered components.

Database pathway: D:\USSL\HYDRUS1D_4\HP1 database\PHREEQC.dat

Solute Transport - Transport Parameters

Bulk D.: **1.5 g/cm³** Disp.: **1 cm** Difus. W. /diffusion coefficient in free water/: **0 cm²/d Note:** Leave other values by default

Solute Transport - Reaction Parameters

Note: Leave all values on default. When using HP 1, all optional values are considered in the PHREEQC module!

Solute Transport Boundary Conditions

Upper Boundary Condition: Concentration Flux BC Lower Boundary Condition: Zero Gradient Solute Concentration: Orgn 0.001 mol/kgw. Note that the value must be in mol per kg water. Other concentrations are 0.

HYDRUS-1D – Profile Information

Menu: Conditions-> Initial Conditions>Pressure Head: Set all points at h = 0 cm **Menu**: Conditions-> Initial Conditions>Observation Points: Insert OP`s at 25, 50 and 100 cm. Leave other options by default.

Menu: File->Save Data Menu: File->Exit

Soil Profile - Summary Button "OK"

II. PHREEQC module settings

Chemical composition and chemical reactions have to be specified in a "Phreeqc.in" file. We recommend using the PHREEQC software for creating the file.



The "Phreeqc.in" file must contain the following data:

and

PHREEQC for Windows - D:\USSL\HYDRUS1D_4\Projects\HP1-October\NITROG\PHREEQC.IN		
<u>File Edit View Calculations H</u> elp		
🗋 📂 🖶 🐁 🖻 🛱 🗙 🌍		
Input Database Grid Chart		
<pre>RATES Orgndegradation -start 10 rem parm(1) first-order degradation coefficient (d-1) 20 rate=parm(1) * tot("water") *mol("Orgn") 30 moles=-rate*time 40 save moles -end SorOrgndegradation -start 10 rem parm(1) first-order degradation coefficient (d-1) 20 rate=parm(1) * tot("water") *mol("SorOrgn") 30 moles=-rate*time 40 care moles</pre>	INVERSE_MODELING ISOTOPES ISOTOPE_ALPHAS ISOTOPE_RATIOS KINETICS KNOBS LLNL_AQUEOUS_MODEL_PARAMETERS MIX NAMED_EXPRESSIONS PHASES PHASES PHIZER PRINT PAAEES REACTION REACTION_TEMPERATURE SAVE OUEDUX	
<pre>40 save moles -end Ammdegradation -start 10 rem parm(1) first-order degradation coefficient (d-1) 20 rate=parm(1)*tot("water")*mol("Amm") 30 moles=-rate*time 40 save moles -end AmmHXdegradation retact</pre>	SELECTED_OUTPUT SOLUTIONS SOLUTION SOLUTION MASTER_SPECIES SOLUTION_SPECIES SOLUTION_SPREAD SURFACE SURFACE SURFACE SURFACE SURFACE SURFACE TITLE TRANSPORT USE USER_GRAPH USER_PRINT	
10 rem parm(1) first-order degradation coefficient (d-1) 20 rate=parm(1)*tot("water")*mol("AmmHX") 30 moles=-rate*time 40 save moles	USER_PUNCH PHREEQC BASIC statements GENERAL BASIC statements	
-end NO3degradation	Defines the rate expression for kinetic reactions in BASIC statements.	
10 rem parm(1) first-order degradation coefficient (d-1)	RATES Quartz -start	
1:1 Insert		

and

PHREEQC for Windows - D:\USSL\HYDRUS1D_4\Projects\HP1-October\NITROG\PHREEQC.IN	m		x		
File Edit View Calculations Help					
Input Database Grid Chart					
<pre>hput Database Grid Chant NO3degradation -start 10 rem parm(1) first-order degradation coefficient (d-1) 20 rate=parm(1)*tot("water")*mol("NO3") 30 moles=-rate*time 40 save moles -end KINETICS 1-101 Orgndegradation -formula Orgn 1.0 Amm -1.0 -parms 0.02 SorOrgndegradation -formula SorOrgn 1.0 Amm -1.0 -parms 0.02 Ammdegradation -formula Amm 1.0 NO3 -1.0 -parms 0.015 NO3degradation -formula AmmHX 1.0 NO3 -1.0 -parms 0.015 NO3degradation -formula NO3 1.0 -parms 0.01</pre>		B - EQUILIBRIUM_PHASES EXCHANGE EXCHANGE_MASTER_SPECIES EXCHANGE_SPECIES GAS_PHASE INCREMENTAL_REACTIONS INVERSE_MODELING ISOTOPES ISOTOPESALPHAS ISOTOPE_ALPHAS ISOTOPE_RATIOS HIL_AQUEOUS_MODEL_PARAMETERS MIX NAMED_EXPRESSIONS PHASES PHASES			
EXCHANGE 1-101		Example: BATES			
x 0.01	Ŧ	Quartz			
<		-start	-		
1:1 Insert			1		

and

PHREEQC for Windows - D:\USSL\HYDRUS1D_4\Projects\HP1-October\NITROG\PHREEQC.IN	
<u>File Edit View Calculations H</u> elp	
🗋 📂 🔚 🐁 🖻 🛱 🗙 🌍	
Input Database Grid Chart	
NO3degradation	EQUILIBRIUM_PHASES
-formula NO3 1.0	
-parms 0.01	EXCHANGE_MASTER_SPECIES
	GAS PHASE
EXCHANGE 1-101	- INCREMENTAL_REACTIONS
-equilibrate 1	INVERSE_MODELING
x 0.01	ISOTOPES
TRANSPORT	
-cells 101	
PRINT	
-reset false	NAMED_EXPRESSIONS
	■ PHASES
SELECTED_OUTPUT	. PITZER
-file PHREEQC.hse	
-reset false	
-time true	
-solution true	
-pH true	Defines the amount and composition of
-totals Orgn Amm N(5) Na K Cl	E exchangers.
-molalities Sororgn Ammita Nax Ka	
	Example:
END	with colution 5
4	EXCHANGE 1-10
1:1 Insert	

In this example:

The new solution species (*Orgn*), and he surface species (*Sor*) are not included in *phreeqc.dat*, so we need to use the PHREEQC keywords: "solution_master_species", "solution_species", "surface_master_species", and "surface_species", to define these new items.

Item	Description (Meaning)	
SOLUTION_MASTER_SPECIES	This keyword is used to define the correspondence between	
	element names and aqueous master species.	
	Element name (this is the name from the listbox), master	
	species (formula for the master species, including its charge),	
Orgn Orgn 0.0 Orgn 1.0	alkalinity, gram formula weight (default value used to convert	
	input data from mass units to mol units) or formula (chemical	
	formula used to calculate gram formula weight), gram formula	
	weight of element.	
SOLUTION_SPECIES	This keyword is used to define chemical reaction and	
	activity-coefficient parameters (k) for each aqueous species.	
	Association reaction for aqueous species. The defined species	
	must be the first species to the right of the equal sign. The	
Olgii – Olgii	association reaction is an identity reaction for each master	
	species.	
log_k 0.0	$\log k$ (note that $\log k$ must be 0.0 for master species, i.e. $k = 1$).	
SOLUTION 1-101	This keyword data block is used to define the temperature and	
	chemical composition of initial solution. The number (1-101)	
	is to designate the following solution composition. (In fact, we	
	must specify the solution/s for all cells of the modeled profile,	
	in our case 100).	
units mol/kgw	Concentration units for the simulation. The default value is	
	mmol/kgw (millimoles per kilogram water).	
Orgn 1e-20	Element list (an element name, which must correspond to the	
Amm 1e-20	items in the first column in SOLUTION MASTER SPECIES)	
N(5) 1e-20	initial concentration (<i>note that it is recommended to enter</i>	
Na 1.0e-03	some very small concentration instead of zero, otherwise the PHREEOC could ignore the component)	
K 1.0e-03		
Cl 2.0e-03		
-water 0.5	Mass of water in the solution in kg (note that the water	
	content expressed in $[L^3L^{-3}]$ in HYDRUS is transferred in	
	PHREEQC in kilogram of water per 1000 cm^3 soil. In fact,	
	every cell of the PHREEQC discretization always has the	
	•	
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	volume of 1000 cm^3 . Practically, the important thing is the	
	ratio of the water and the entire node/cell volume, which has	
	to be the same both for a node (HYDRUS) and for a cell	
	(PHREEQC).	
	This keyword data block is used to define the correspondence	
SURFACE_MASTER_SPECIES	between surface binding-site names and surface master	
	species.	
	Surface binding-site name (name of a surface binding site),	
Sor Sor	surface master species (formula for the surface master	
	species).	
	This keyword is used to define a reaction and $\log K$ for each	
SURFACE_SPECIES	surface species, including surface master species.	
	Association reaction for surface species. The defined species	
Sor = Sor	must be the first species to the right of the equal sign. It is an	
	identity reaction for the master species.	
log_k 0.0	log k (note that log k for a master species is 0.0).	
	Association reaction for the mass action equation for the linear	
	adsorption (<i>note that</i> as we use surface complexation reaction,	
Sor + Orgn = SorOrgn	<i>here is the place for the reaction</i>). Note that the dimension of	
	SorOrgn is mol/kgw.	
log_k -99.125	$log k$ (note that $k = K_{dl}^{w}$). $K_{dl}^{w} = K_{d,l*}\rho_b/[Sor]$	
	This keyword is used to define the amount and composition of	
SURFACE 1-101	each surface in a surface assemblage	
	Number ("-equilibrate" indicates that the surface assemblage	
	is defined to be in equilibrium with a given solution	
-equilibrate 1	<i>composition</i>). number (solution number with which the surface	
	assemblage is to be in equilibrium)	
	Surface binding-site name (name of the surface binding site).	
	sites (total number of sites for this binding site, in moles).	
Sor 1e100 1 1e100	specific area per gram (specific area of surface, in m^2/g).	
	mass (mass of solid for calculation of surface area, in g:	
	surface area is "mass" times "specific area per gram").	
	This keyword data block is used to define mathematical rate	
	expressions for kinetic reactions. Note that general rate	
RATES	formulas are defined in the RATES data block and specific	
	parameters for transport kinetics are defined in the KINETICS	
	data block.	
Orgndegradation	name of rate expression – alphanumeric character string that	
015h005h000h	mane of two expression alphanemetre enalacter string that	

	identifies the rate expression.
-start	identifier marks the beginning of a BASIC program by which
	the moles of reaction for a time subinterval are calculated.
	BASIC language program is written from lines 10 to 40.
10 new new (1) first order degradation	numbered BASIC statement – rem is only a comment (without
acofficient (d 1)	effect on the calculations) indicating the meaning of the first
coefficient (d-1)	parameter, which is first-order degradation coefficient
	numbered BASIC statement - rate defines the rate of
	degradation in the liquid phase, $parm(1)$ is the first-order rate
20 rate= <i>parm</i> (1)* <i>tot</i> ("water")* <i>mol</i> ("Orgn")	constant, tot("water") and mol("Orgn") are the amounts of
	water and solute concentration in the cell.
	numbered BASIC statement - moles integrates the rate over
	the time subinterval with the special variable time. Note that
	the negative sign results in a negative amount of moles saved
30 moles=-rate* <i>time</i>	in the last statement (line 40). In general, a negative sign
	means that elements will be removed from the solution (i.e.
	precipitation, degradation, or decay).
40	numbered BASIC statement – save the moles of reaction
40 save moles	during the time interval are saved
	Identifier marks the end of the BASIC program by which the
	number of moles of a reaction for a time subinterval is
-end	calculated. Note the hyphen is required to avoid a conflict with
	the keyword END.
	name of rate expression – alphanumeric character string that
SorOrgndegradation	identifies the rate expression. In this case, it represents the
	degradation of the solid (adsorbed) phase of the component.
	identifier marks the beginning of a BASIC program by which
-start	the moles of reaction for a time subinterval are calculated.
	BASIC language program is written from lines 10 to 40.
	numbered BASIC statement – rem is only a comment (without
10 rem parm(1) first-order degradation	effect on the calculations) indicating the meaning of the first
coefficient (d-1)	parameter, which is first-order degradation coefficient
20 rate= <i>parm</i> (1)* <i>tot</i> ("water")* <i>mol</i> ("SorOrgn")	numbered BASIC statement - rate defines the rate of
	degradation in the solid phase, parm(1) is the first-order rate
	constant, tot("water") and mol("SorOrgn") are the amounts of
	water and adsorbed concentration in the cell. Note that, as we
	defined the adsorbed concentration ("SorOrgn") in mol/kgw,
	this equation is the same as the equation in "Orgndegradation"

	data block.
30 moles=-rate* <i>time</i>	numbered BASIC statement – moles integrates the rate over
	the time subinterval with the special variable time. Note that
	the negative sign results in a negative amount of moles saved
	in the last statement (line 40). In general, a negative sign
	means that elements will be removed from the solution (i.e.
	precipitation, degradation, or decay).
40 save moles	numbered BASIC statement – save the moles of reaction
	during the time interval are saved
	Identifier marks the end of the BASIC program by which the
hand	number of moles of a reaction for a time subinterval is
-епа	calculated. Note the hyphen is required to avoid a conflict with
	the keyword END.
Ammdegradation	the same as for the Orgndegradation data block
-start	the same as for the Orgndegradation data block
10 rem parm(1) first-order degradation	the same as for the Orgndegradation data block
coefficient (d-1)	
20 rate=parm(1)*tot("water")*mol("Amm")	the same as for the Orgndegradation data block
30 moles=-rate* <i>time</i>	the same as for the Orgndegradation data block
40 save moles	the same as for the Orgndegradation data block
-end	the same as for the Orgndegradation data block
AmmHXdegradation	the same as for the SorOrgndegradation data block
-start	the same as for the SorOrgndegradation data block
10 rem parm(1) first-order degradation	the same as for the SorOrgndegradation data block
coefficient (d-1)	
20 rate= <i>parm</i> (1)* <i>tot</i> ("water")* <i>mol</i> ("AmmHX")	the same as for the SorOrgndegradation data block
30 moles=-rate* <i>time</i>	the same as for the SorOrgndegradation data block
40 save moles	the same as for the SorOrgndegradation data block
-end	the same as for the SorOrgndegradation data block
NO3degradation	the same as for the Orgndegradation data block
-start	the same as for the Orgndegradation data block
10 rem parm(1) first-order degradation	the same as for the Orgndegradation data block
coefficient (d-1)	
20 rate= <i>parm</i> (1)* <i>tot</i> ("water")* <i>mol</i> ("NO3")	the same as for the Orgndegradation data block
30 moles=-rate* <i>time</i>	the same as for the Orgndegradation data block
40 save moles	the same as for the Orgndegradation data block
-end	the same as for the Orgndegradation data block
KINETICS 1-101	This keyword data block is used to identify kinetic reactions

and to specify reaction parameters to a specific cell. The
number (1-101) is to designate the following set of kinetic
reactions to the number of cells.
<i>name of rate expression</i> . The rate name must correspond to the
RATES data block
Chemical formula or the name of the phase to be added by the
kinetic reaction, Orgn; stoichiometric coefficient 1, defines
the mole transfer coefficient for formula per mole of reaction
progress evaluated by the rate expression in RATES). Note
that the user should identify which solution species appear or
disappear. The stoichiometric coeff. "1.0" after the Orgn has
positive sign which means Orgn disappears. The
stoichiometric coeff. "-1.0" after the <i>Amm</i> represents the mole
transfer coefficient and the sign is negative which means Amm
appears.
<i>list of parameters</i> –defining parameters in the rate expression,
note that the dimension of the parameter (day ⁻¹) is defined in
the HYDRUS Time Information window.
<i>name of rate expression</i> . The rate name must correspond to the
RATES data block
Chemical formula or the name of the phase to be added by the
kinetic reaction, SorOrgn; stoichiometric coefficient 1,
defines the mole transfer coefficient for formula per mole of
reaction progress evaluated by the rate expression in RATES).
Note that the user should identify which species appear or
disappear. The stoichiometric coeff. "1.0" after the SorOrgn
has positive sign which means SorOrgn disappears. The
stoichiometric coeff. "-1.0" after the <i>Amm</i> represents the mole
transfer coefficient and the sign is negative which means Amm
appears.
<i>list of parameters</i> –defining parameters in the rate expression,
note that the dimension of the parameter (day ⁻¹) is defined in
the HYDRUS Time Information window.
<i>name of rate expression</i> . The rate name must correspond to the
RATES data block
Chemical formula or the name of the phase to be added by the
kinetic reaction, Amm; stoichiometric coefficient 1, defines

	progress evaluated by the rate expression in RATES). Note
	that the user should identify which solution species appear or
	disappear. The stoichiometric coeff. "-1.0" represents the mole
	transfer coefficient.
	list of parameters -defining parameters in the rate expression,
-parms 0.015	note that the dimension of the parameter (day ⁻¹) is defined in
	the HYDRUS Time Information window.
AmmHXdegradation	name of rate expression. The rate name must correspond to the
	RATES data block
	Chemical formula or the name of the phase to be added by the
	kinetic reaction, AmmHX; stoichiometric coefficient 1,
	defines the mole transfer coefficient for formula per mole of
	reaction progress evaluated by the rate expression in RATES).
	Note that the user should identify which species appear or
-tormula AmmHX I NO3 -1.0	disappear. The stoichiometric coeff. "1.0" after the AmmHX
	has positive sign which means AmmHX disappears. The
	stoichiometric coeff. "-1.0" after the NO3 represents the mole
	transfer coefficient and the sign is negative which means NO3
	appears.
	list of parameters -defining parameters in the rate expression,
-parms 0.015	note that the dimension of the parameter (day ⁻¹) is defined in
	the HYDRUS Time Information window.
NO21 and the second	name of rate expression. The rate name must correspond to the
NOSdegradation	RATES data block
	Chemical formula or the name of the phase to be added by the
	kinetic reaction, Contc; stoichiometric coefficient 1, defines
-formula NO3 I	the mole transfer coefficient for formula per mole of reaction
	progress evaluated by the rate expression in RATES).
	list of parameters -defining parameters in the rate expression,
-parms 0.010	note that the dimension of the parameter (day ⁻¹) is defined in
	the HYDRUS Time Information window.
EXCHANGE 1-101	This keyword data block is used to define the amount and
	composition of an assemblage of exchangers. 1-101 is the
	positive number to designate the following exchange
	assemblage and its composition. In our case we define the
	same exchanger for all nodes, namely exchange site X
-equilibrate 1	"-equilibrate" indicates that the exchange assemblage is
	defined to be in equilibrium with a given solution

	composition), number (solution number with which the surface
	assemblage is to be in equilibrium).
	Exchange site (only the name of the exchange site needs to be
V 0.01	entered), amount (quantity of exchange site, in moles). Note
X 0.01	that the dimension is by default always in moles. This means
	that every cell possesses 0.01 mol of the exchanger.
	This key data block is used to simulate 1D transport processes.
	However, this option is not used in HP 1 but for spatial
TRANSPORT	integration (integration of the profile) and connection with the
	transport module (HYDRUS) only the number of cell needs to
	be specified.
	Indicates the number of the cells in the profile (note that this
-cells 101	number must be equal to the number of nodes determined in
	the HYDRUS module).
	This keyword data block is used to select which results are
PRINT	written to the output file.
	Changes all print options (identifiers) listed on lines 2 through
	15 to true or false (see PHREEQC Manual, p. 120). If false is
-reset false	used all data blocks on line 2 through line 15 will NOT be
	printed in the output file.
	This keyword data block is used to produce a file* that is
SELECTED_OUTPUT	suitable for processing by spreadsheets and other
	data-management software.
	"-file" (identifier allows definition of the name of the file
	where the selected initial information (results) will be written),
-file PHREEQC.hse	file name (file name where selected results will be written).
	Note: the file name may have extensions "*.hse", "*.out", or
	"*.sel".
	Change print options for all identifiers from line 6 to line 20 (if
-reset false	the statement "false" is used only the identifiers marked "true"
	will be printed (see PHREEQC Manual, p. 137)
	Prints to the selected-output file* the cumulative transport
-time true	time since the beginning of the run or other defined options.
-solution true	Prints solution number used for the calculation in each line of
	the selected-output file.
-totals Orgn Amm N(5) Na K Cl	Element list ("-totals" is an identifier allows definition of a list
	of total concentrations [mol/kgw] that will be written to the
	selected-output file) element list (list of elements for which

	total concentrations will be written).
-molalities SorOrgn AmmHX NaX KX	Species list ("-molalities" is an identifier allows definition of
	a list of species for which concentrations [mol/kgw] will be
	written to the selected-output file), species list (list of aqueous,
	exchange, or surface species for which concentrations will be
	written to the selected-output file).
END	This keyword ends the data input for a simulation

Note: For more information see the PHREEQC Manual for the relevant topic.

Go back to HYDRUS-1D GUI and execute HP1. When the program finishes, open the NITROG folder:

HP 1 creates specific files in which the final results are stored. Get the species results from the "nod_inf_chem.out" and "obs_nod_chem.out" files. Note that for each observation node there is a separate output file.

Results can also be received from HYDRUS 1D output files:

Post-processing

Observation Points



These graphs show the Na^+ (green), *Cl* (black), K^+ (red), and Ca^{2+} (blue) concentrations according to the time at the bottom of the profile.

Profile Information



The *Orgn* concentration in the solute phase through the profile at the initial time (the black graph) and at the printed time steps.

The ammonium ion concentration in the solute phase through the profile at the initial time (the black graph) and at the printed time steps.



The nitrate ion concentration in the solute phase through the profile at the initial time (the black graph) and at the printed time steps.





The Na^+ concentration in the solute phase through the profile at the initial time (the black graph) and at the printed time steps. The K^+ concentration in the solute phase through the profile at the initial time (the black graph) and at the printed time steps.



