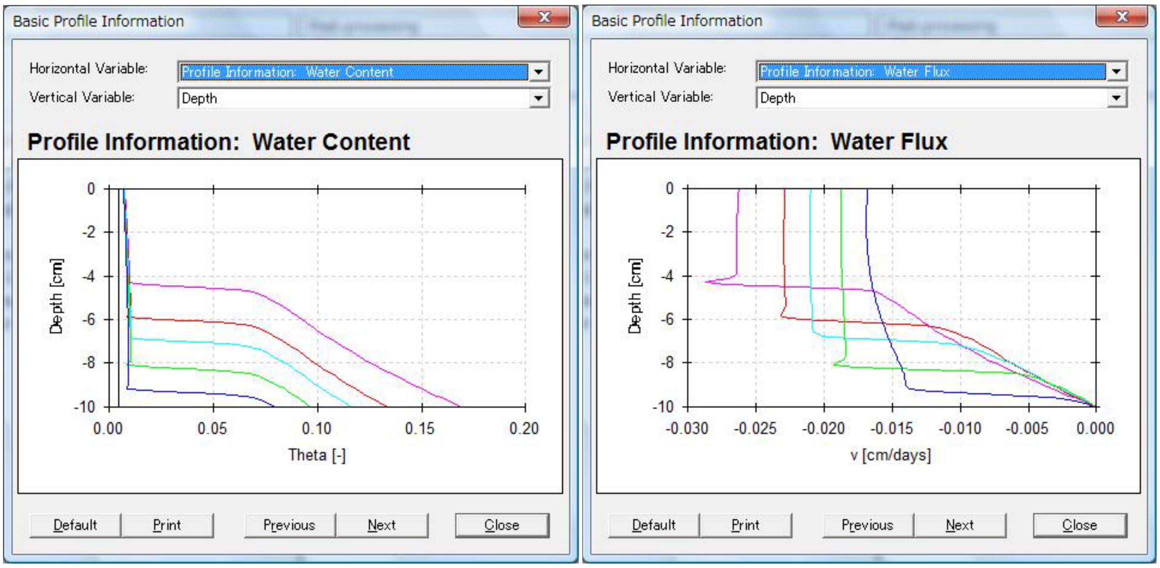
第 47 回　農業農村工学会　土壌物理研究部会　研究集会

HYDRUS-1D の新機能の紹介と今後の展開


Basic Profile Information

Horizontal Variable: Profile Information: Water Content
Vertical Variable: Depth

Profile Information: Water Content

Basic Profile Information

Horizontal Variable: Profile Information: Water Flux
Vertical Variable: Depth

Profile Information: Water Flux

平成 20 年 10 月 19 日（日）

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

平成20年度土壌物理研究部会（農業農村工学会）研究集会

HYDRUS-1Dの新機能の紹介と今後の展開

とき：2008年10月18日（日）9:00～16:00

ところ：三重大学　三翠ホール

開会挨拶　三重大学　取出伸夫部会長　9:00－ 9:10

1．HYDRUS-1Dの新機能とその適用事例（演習）　9:10－10:10

－土中液状水・水蒸気・熱同時移動－

東京農工大学　斎藤広隆

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　10:20－11:10

三重大学　取出伸夫・陳代文・Dimitar Antonov

3. HP1を用いた形態変化を伴う土中の窒素移動（演習）　11:20－13:50

三重大学　取出伸夫・Dimitar Antonov　（途中昼休み）

4．マルチステップ法による水分移動特性の推定　14:00－14:30

鳥取大学　井上光弘

5. 負圧浸入計による表層土の水分移動特性の推定　14:30－15:00

東京農工大学大学院連合農学研究科　朝田景

6. 自由討論　15:10－15:55

岡山大学　諸泉利嗣

閉会挨拶　明治大学　登尾浩助（次期部会長）

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「HYDRUS-1Dの新機能の紹介と今後の展開」開催に当たって

農業農村工学会土壌物理研究部会長　取 出　伸　夫

土壌物理の対象の中心が実験室内の土カラムからフィールドへ移り，さらに農地の水管理問題からより広く土壌環境圏の物質移動問題へと発展していく中，土壌物理学の長年の研究の蓄積の成果として，土中の水分・溶質移動汎用予測プログラムの整備が進められてきました。土壌物理研究部会では，汎用水分・溶質移動予測プログラムHYDRUSの開発やその利用に携わる数名の有志によりHYDRUSグループを立ち上げ，汎用プログラムHYDRUSの応用と普及に努めてきました。昨年度の研究集会においては,「不飽和土中の水分・溶質移動モデルの研究と普及」と題して，研究と応用の両面から議論を行い, また汎用プログラムの適用事例や今後の可能性に関して情報交換を行いました。今年度は, 6月にHYDRUSの開発者であるカリフォルニア大学リバーサイド校Jirka Simunek教授を招へいし，東京農工大学と東京大学において4日間にわたるHYDRUS講習会とHYDRUSワークショップを開催しました。近隣アジア諸国からも含めて100名近い参加者があり，改めて，モデルや数値計算予測に対する需要と期待の高さを感じ，研究集会や講習会の継続の必要性を痛感しました。

そこで本年度の研究集会においては，「HYDRUS-1Dの新機能の紹介と今後の展開」と題し，主にHYDRUSグループにおける取り組みを紹介しながら議論を行うことにしました。まず，version 4として今春に公開されたHYDRUS-1Dの新機能について概説し，さらに液状水・水蒸気・熱同時移動と多成分化学物質移動予測プログラムHP1について，出入力画面を示しながらの演習も含めて解説します。そして水分移動特性の逆解析の実験室と野外現場における適用について紹介します。その上で，今後の研究，教育，現場への応用に関する議論を行いたいと考えています。

この研究集会が，不飽和土中の水分・溶質移動モデル開発や普及に関する情報交換の場となり，また異なる立場の方々の共同研究に貢献できることを期待しています。ご意見，ご要望をHYDRUSグループ(hydrus-grp@bio.mie-u.ac.jp)にお寄せ頂ければ幸いです。

目　次

HYDRUS-1Dの新機能とその適用事例（演習）

H20.10.19 農業農村工学会土壌物理研究部会

斎藤広隆[1), 坂井勝[2), 取出伸夫[3), Jiri Simunek[2)
1) 東京農工大学共生科学技術院
2) カリフォルニア大学リバーサイド校環境科学科
3) 三重大学大学院生物資源学研究科

HYDRUS-1D Ver. 4- 新機能

- ◆**液状水・水蒸気・熱同時移動**
- ◆**Dual porosityモデルによる水分流れと溶質移動（平衡・非平衡吸着）**
- ◆**Dual-permeabilityモデルによる水分流れと溶質移動（平衡・非平衡吸着）**
- ◆**Penman-Monteith式あるいはHargreaves式による可能蒸発散量の計算**
- ◆**蒸発量，発散量，降雨量の時間変化**
- ◆**HP1のサポート**

土中液状水・水蒸気移動

$$q_{Liquid} = q_{Lh} + q_{LT} = \underbrace{-K_{Lh}(h)\frac{\partial h}{\partial z} - K_{Lh}(h)}_{\text{等温液状水フラックス}} \underbrace{- K_{LT}(T)\frac{\partial T}{\partial z}}_{\text{非等温液状水フラックス}}$$

$$q_{vapor} = q_{vh} + q_{vT} = \underbrace{-K_{vh}(h)\frac{\partial h}{\partial z}}_{\text{等温水蒸気フラックス}} \underbrace{- K_{vT}(T)\frac{\partial T}{\partial z}}_{\text{非等温水蒸気フラックス}}$$

(Philip and de Vries, 1957)

修正リチャーズ式

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial t}\left[K_{Lh}\frac{\partial h}{\partial z} + K_{Lh} + K_{LT}\frac{\partial T}{\partial z} + K_{vh}\frac{\partial h}{\partial z} + K_{vT}\frac{\partial T}{\partial z}\right] - S$$

土中熱移動

$$q_h = \overset{(1)}{-\lambda(\theta)\frac{\partial T}{\partial z}} + \overset{(2)}{C_w T q_L} + \overset{(3)}{C_v T q_v} + \overset{(4)}{L_0 q_v}$$

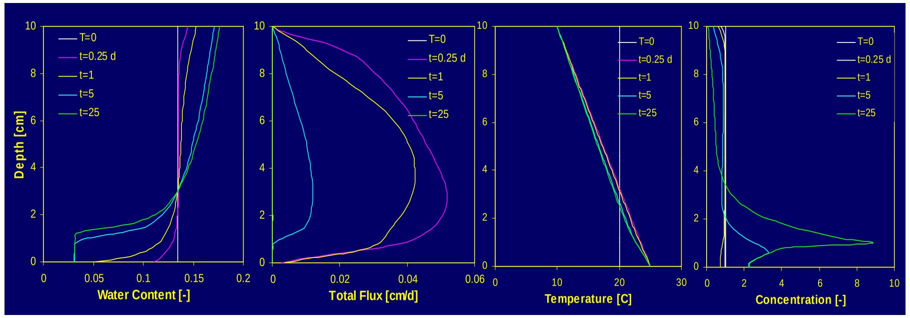
(1) 伝導による顕熱輸送
(2) 液状水による顕熱輸送
(3) 水蒸気による顕熱輸送
(4) 水蒸気による潜熱輸送

熱移動の基礎方程式

$$\frac{\partial C_p}{\partial t} + L_0\frac{\partial \theta_v}{\partial t} = \frac{\partial}{\partial z}\left[\lambda(\theta)\frac{\partial T}{\partial z}\right] - C_w\frac{\partial q_L T}{\partial z} - L_0\frac{\partial q_v}{\partial z} - C_v\frac{\partial q_v T}{\partial z} - C_w S T$$

λ: 見かけ熱伝導率, C_w: 水の体積熱容量, C_v: 水蒸気の体積熱容量, L_0: 水の蒸発潜熱, C_p: 土の体積熱容量, S: 根の吸水などのよる熱損失

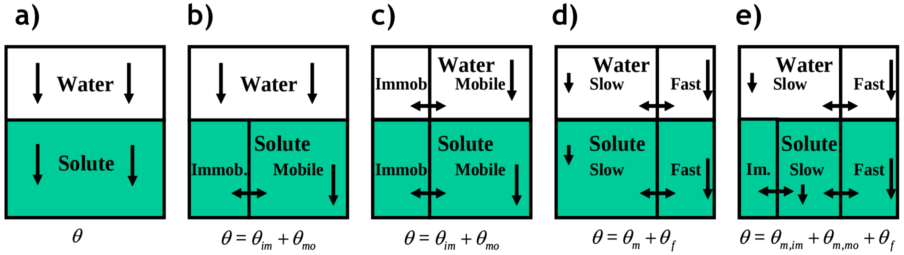
液状水・水蒸気・熱同時移動



Total flux=water flux+vapor flux

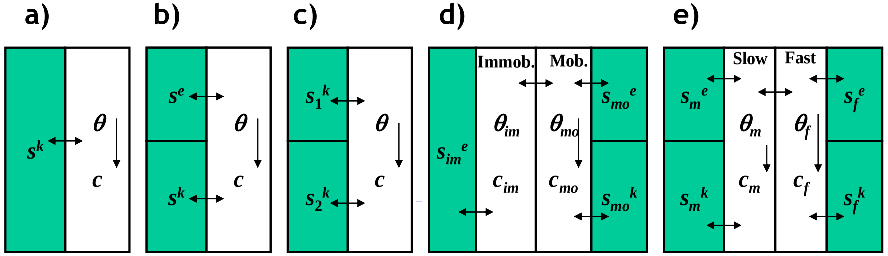
Nassar & Horton (1992)

物理的非平衡モデル



a) Uniform flow
b) Mobile-Immobile or MIM
c) Dual-Porosity
d) Dual-Permeability
e) Dual-Permeability with MIM in the Matrix Region

化学的非平衡溶質移動モデル



a) One-Site Kinetic Model
b) Two-Site Model (kinetic and instantaneous sorption)
c) Two-Site Kinetic Model
d) Dual-Porosity with One Kinetic Site Model
e) Dual-Permeability with Two-Site Model

Penman-Monteith Equation

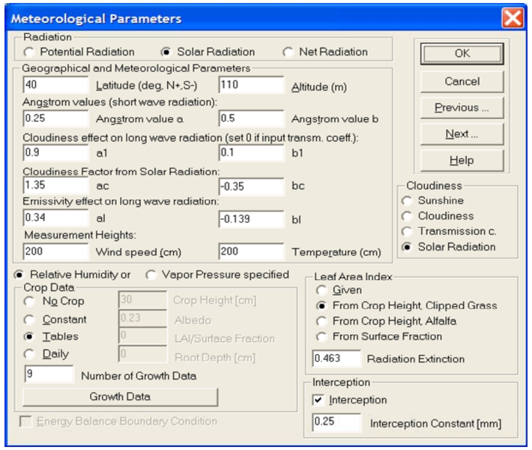
The Penman-Monteith combination method for calculating of reference evapotranspiration [FAO, 1990]:

$$ET_0 = ET_{rad} + ET_{aero} = \frac{1}{\lambda}\left[\frac{\Delta(R_n - G)}{\Delta + \gamma(1 + r_c / r_a)} + \frac{\rho c_p (e_a - e_d) / r_a}{\Delta + \gamma(1 + r_c / r_a)}\right]$$

ET_o - reference crop evapotranspiration [mm d^{-1}]
ET_{rad} - radiation term [mm d^{-1}]
ET_{aero} - aerodynamic term [mm d^{-1}]
R_n - net radiation at crop surface [MJ m^{-2}d^{-1}]
G - soil heat flux [MJ m^{-2}d^{-1}]
$(e_a - e_d)$ - vapour pressure deficit [kPa]
Δ - slope vapour pressure curve [kPa °C^{-1}]

γ - psychrometric constant [kPa °C^{-1}]
λ - latent heat of vaporization [MJ kg^{-1}]
ρ - atmospheric density [kg m^{-3}]
c_p - specific heat of moist air [i.e., 1.013 kJ kg^{-1} °C^{-1}]
e_a - saturation vapor pressure at temperature T [kPa],
e_d - actual vapor pressure [kPa]
r_c - crop canopy resistance [s m^{-1}]
r_a - aerodynamic resistance [s m^{-1}]

Graphical User Interface for Meteorological Information



Meteorological Parameters

Radiation
○ Potential Radiation ● Solar Radiation ○ Net Radiation

Geographical and Meteorological Parameters
40 Latitude (deg, N+,S-) 110 Altitude (m)
Angstrom values (short wave radiation):
0.25 Angstrom value a 0.5 Angstrom value b
Cloudiness effect on long wave radiation (set 0 if input transm. coeff.):
0.9 a1 0.1 b1
Cloudiness Factor from Solar Radiation:
1.35 ac -0.35 bc
Emissivity effect on long wave radiation:
0.34 al -0.139 bl
Measurement Heights:
200 Wind speed (cm) 200 Temperature (cm)

Cloudiness
○ Sunshine
○ Cloudiness
○ Transmission c.
● Solar Radiation

● Relative Humidity or ○ Vapor Pressure specified

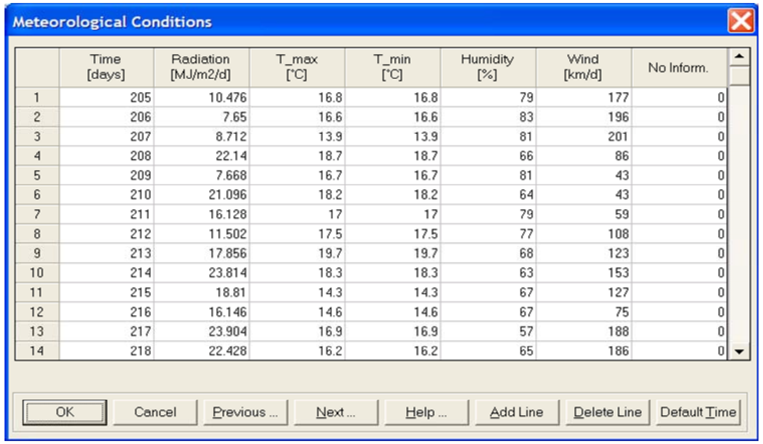
Crop Data
○ No Crop 30 Crop Height [cm]
○ Constant 0.23 Albedo
● Tables 0 LAI/Surface Fraction
○ Daily 0 Root Depth [cm]
9 Number of Growth Data

Leaf Area Index
○ Given
● From Crop Height, Clipped Grass
○ From Crop Height, Alfalfa
○ From Surface Fraction
0.463 Radiation Extinction

Interception
☑ Interception
0.25 Interception Constant [mm]

☐ Energy Balance Boundary Condition

Graphical User Interface for meteorological information



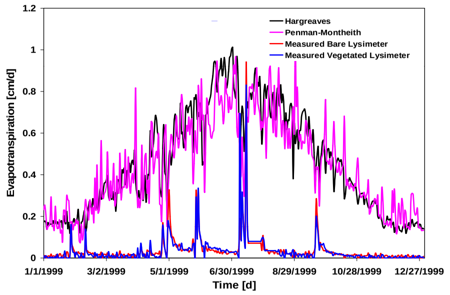
Meteorological Conditions

	Time [days]	Radiation [MJ/m2/d]	T_max [°C]	T_min [°C]	Humidity [%]	Wind [km/d]	No Inform.
1	205	10.476	16.8	16.8	79	177	0
2	206	7.65	16.6	16.6	83	196	0
3	207	8.712	13.9	13.9	81	201	0
4	208	22.14	18.7	18.7	66	86	0
5	209	7.668	16.7	16.7	81	43	0
6	210	21.096	18.2	18.2	64	43	0
7	211	16.128	17	17	79	59	0
8	212	11.502	17.5	17.5	77	108	0
9	213	17.856	19.7	19.7	68	123	0
10	214	23.814	18.3	18.3	63	153	0
11	215	18.81	14.3	14.3	67	127	0
12	216	16.146	14.6	14.6	67	75	0
13	217	23.904	16.9	16.9	57	188	0
14	218	22.428	16.2	16.2	65	186	0

Hargreaves Equation

$$ET_p = 0.0023 R_a \left(T_m + 17.8\right)\sqrt{TR}$$

R_a - extraterrestrial radiation in the same units as ET_p [e.g., mm d^{-1} or J m^{-2}s^{-1}]
T_m - daily mean air temperature [°C]
TR - temperature range between the mean daily maximum and minimum [°C]

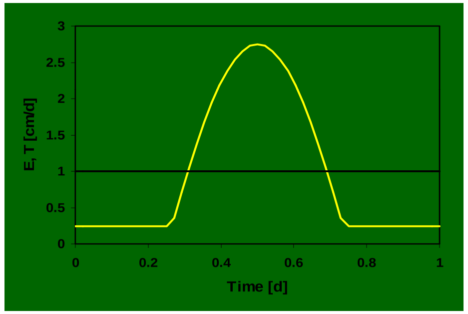


蒸発･蒸散量の日変化

$$T_p(t) = 0.24\overline{T_p} \qquad t < 0.264\text{d},\ t > 0.736\text{d}$$

$$T_p(t) = 2.75\overline{T_p}\sin\left(\frac{2\pi t}{1\text{day}} - \frac{\pi}{2}\right) \qquad t \in (0.264\text{d}, 0.736\text{d})$$

Hourly values between 0-6 a.m. and 18-24 p.m. represent 1% of the total daily value and a sinusoidal shape is followed during the rest of the day (Fayer, 2000)



HP1 (Jacques and Šimůnek, 2005)

Coupled HYDRUS-1D and PHREEQC

HYDRUS-1D [Šimůnek et al., 2008]:

- Variably Saturated Water Flow
- Solute Transport
- Heat transport
- Root water uptake

PHREEQC [Parkhurst and Appelo, 1999]:

Available chemical reactions:

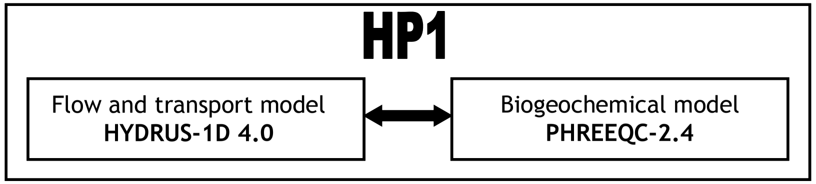
- Aqueous complexation
- Redox reactions
- Ion exchange (Gains-Thomas)
- Surface complexation - diffuse double-layer model and non-electrostatic surface complexation model
- Precipitation/dissolution
- Chemical kinetics
- Biological reactions

Simulation Tool HP1

Simulating water flow, transport and bio-geochemical reactions in environmental soil quality problems

HP1

A Coupled Numerical Code for Variably Saturated Water Flow, Solute Transport and Biogeochemistry in Soil Systems



HP1

Flow and transport model
HYDRUS-1D 4.0

Biogeochemical model
PHREEQC-2.4

The HYDRUS (Unsaturated Flow) Package for MODFLOW-2000

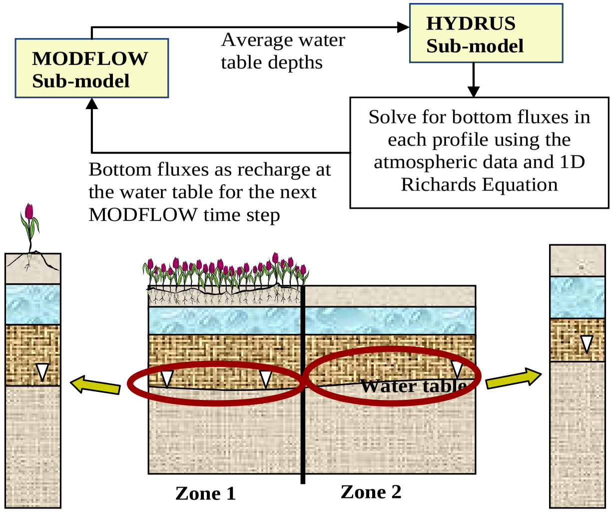
Hyeyoung Sophia Seo, Jirka Šimůnek, Eileen P. Poeter

Colorado School of Mines, 1500 Illinois St. Golden CO 80401

University of California, Riverside

Seo, H. S., J. Šimůnek, and E. P. Poeter, Documentation of the HYDRUS Package for MODFLOW-2000, the U.S. Geological Survey Modular Ground-Water Model, *GWMI 2007-01*, International Ground Water Modeling Center, Colorado School of Mines, Golden, Colorado, 96 pp., 2007.

Twarakavi, N. K. C., J. Šimůnek, and H. S. Seo, Evaluating interactions between groundwater and vadose zone using HYDRUS-based flow package for MODFLOW, *Vadose Zone Journal*, Special Issue "Vadose Zone Modeling", *7*(2), 757-768, 2008.



MODFLOW Sub-model

Average water table depths

HYDRUS Sub-model

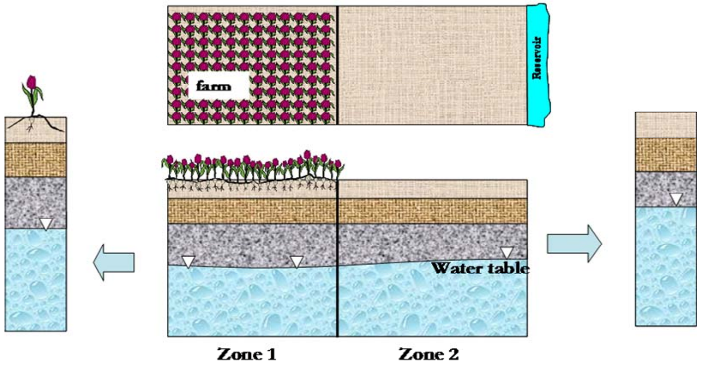
Solve for bottom fluxes in each profile using the atmospheric data and 1D Richards Equation

Bottom fluxes as recharge at the water table for the next MODFLOW time step

HYDRUS Package: Zoning

MODFLOW model domain is grouped in to zones based on similarities in soil hydraulic characteristics, hydrogeology and meteorology.

A HYDRUS vertical profile is assigned to each of the zones on which the 1D Richards equation is used.



水蒸気凝縮実験（宮﨑，1976）への適用

H20.10.19　農業農村工学会土壌物理研究部会

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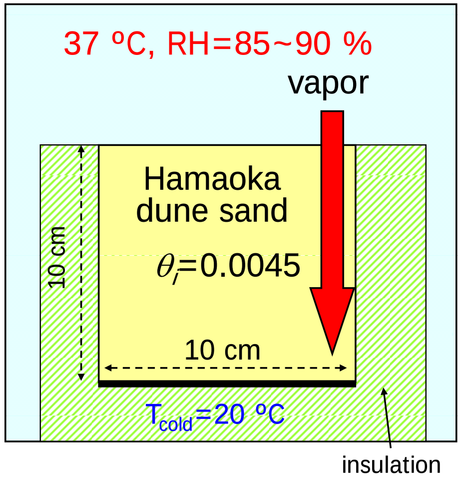
1)　カリフォルニア大学リバーサイド校環境科学科

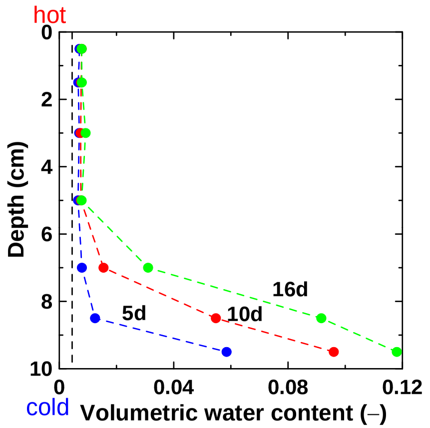
2)　東京農工大学共生科学技術院

3)　三重大学大学院生物資源学研究科

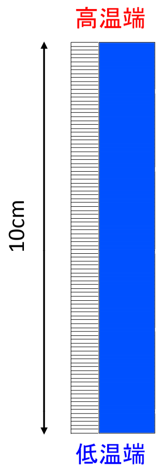
UC RIVERSIDE　TAT 東京農工大学　bio. Mie University

凝縮実験：宮﨑（1976）





数値計算：HYDRUS-1D



初期条件

θ_i=0.0045, T_i=23.5 °C

水分移動境界条件

上端:　$q_{top} = q_{liquid} + q_{vapor} = q_{observed}$

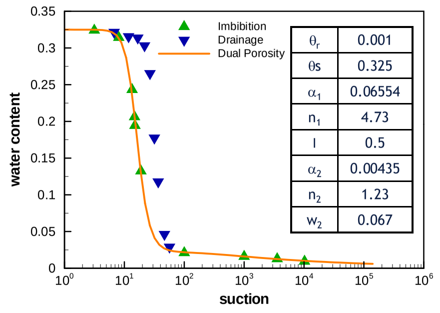
下端:　$q_{bottom} = q_{liquid} + q_{vapor} = 0$

熱移動境界条件

$T_{top} = 36.3\ ^{\circ}\mathrm{C}\ \ T_{bottom} = 23.5\ ^{\circ}\mathrm{C}$（実測値）

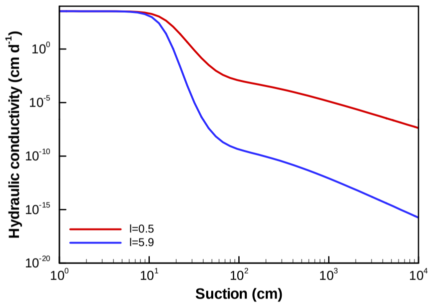
Dual Porosity Model

水分特性曲線



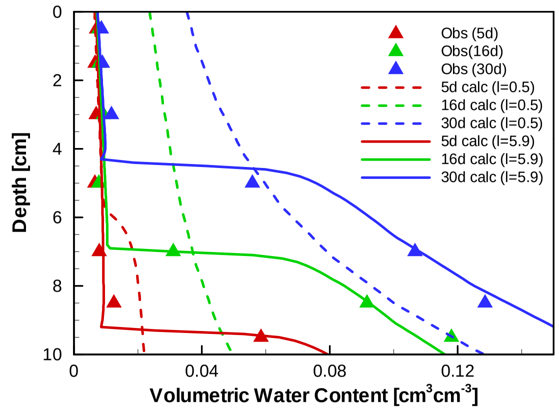
θ_r	0.001
θs	0.325
α_1	0.06554
n_1	4.73
l	0.5
α_2	0.00435
n_2	1.23
w_2	0.067

不飽和透水係数



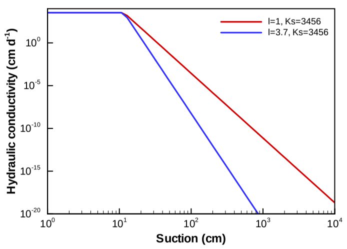
$$S_e(h)=\frac{\theta(h)-\theta_r}{\theta_s-\theta_r}=\sum_{i=1}^{k} w_i\left[1+\left(\alpha_i|h|\right)^{n_i}\right]^{-m_i} \quad K(\theta)=K_s\left(\sum_{i=1}^{k} w_i S_{e_i}\right)^{l}\frac{\left(\sum_{i=1}^{k} w_i\alpha_i\left[1-\left(1-S_{e_i}^{1/m_i}\right)^{m_i}\right]\right)^2}{\left(\sum_{i=1}^{k} w_i\alpha_i\right)^2}$$

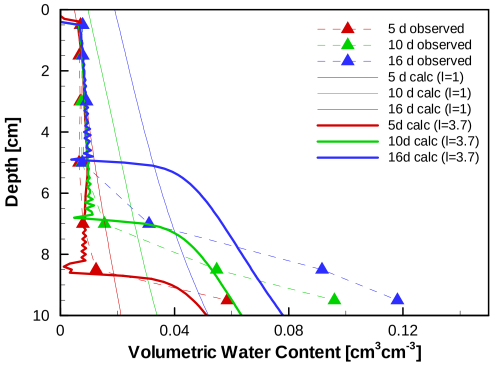
水分分布：Dual Porosity



Brooks & Corey Model

$$K(h)=K_s S_e^{\,2/n+l+2}$$

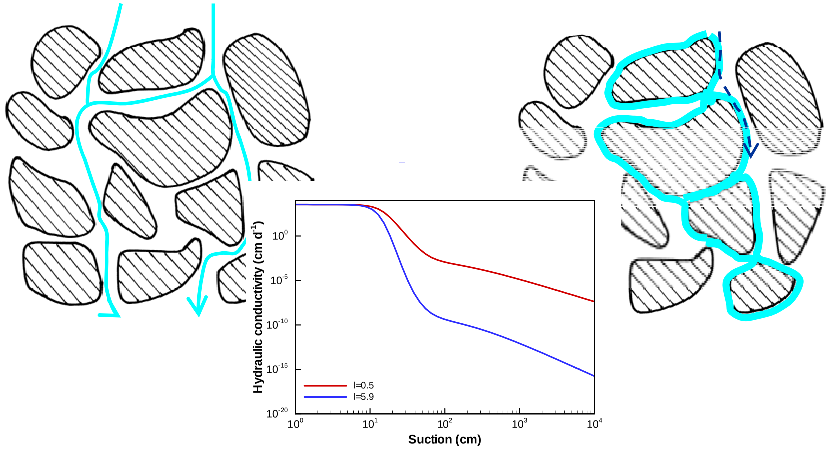




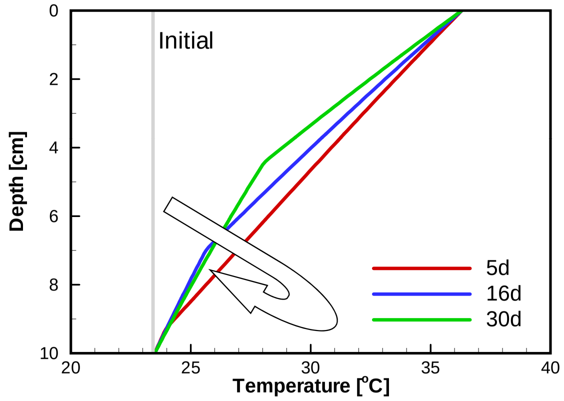
流れの形態

高圧力：間隙流

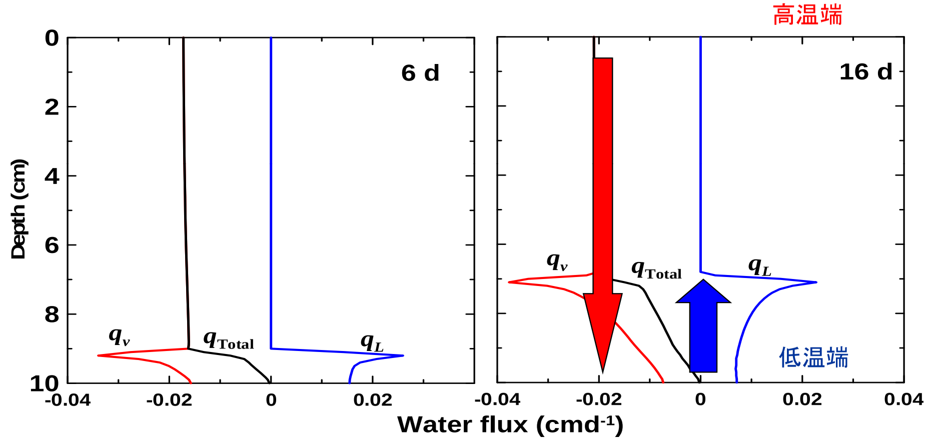
低圧力：膜流



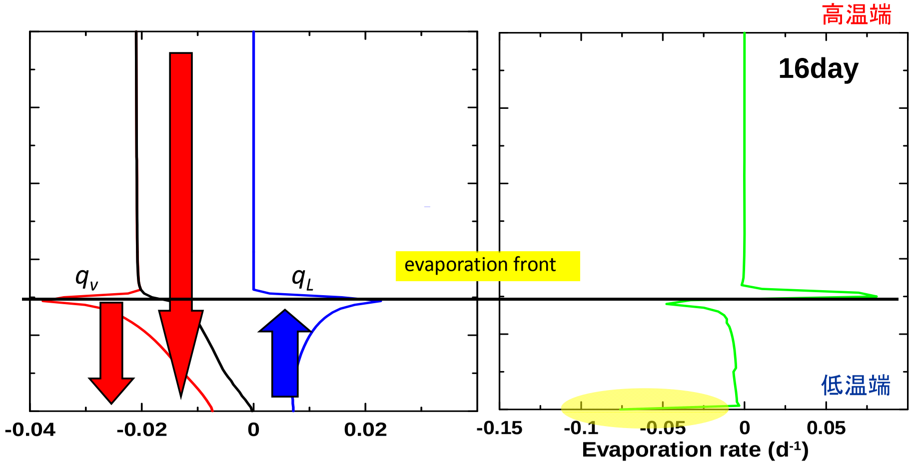
温度分布



水分フラックス分布



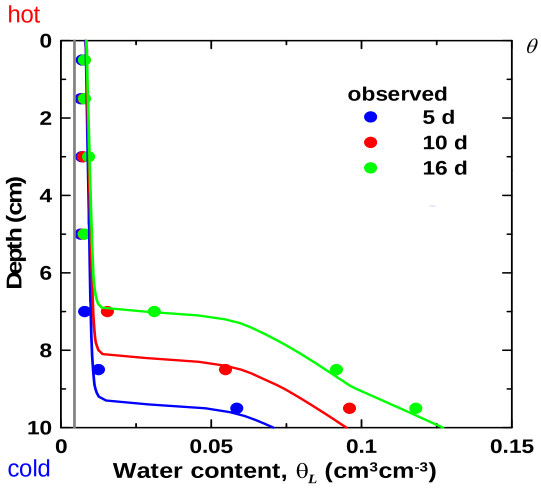
蒸発と凝縮



まとめ

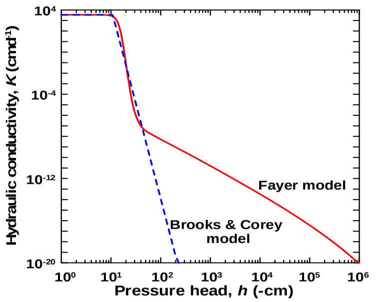
- 非等温下の砂丘砂における水蒸気凝縮過程の数値計算から，砂丘砂の低水分（低圧力）領域の水分移動の形態について，間隙流とは異なると推察された。
- Dual Porosityモデルを用いることで，形態の異なる流れ（間隙流・膜流）を表現し，低水分領域の不飽和透水係数の推定が大きく向上した。
- 数値計算により，4成分の水分フラックス，凝縮，蒸発速度を定量的に評価できた。水蒸気と液状水は，相変化を繰り返しながら試料内を循環していることを示すことができた。

Fayerモデル（坂井ら, 2008）



$$\theta = \chi(h)\theta_a + \left(\theta_s - \chi(h)\theta_a\right)\left[1 + (\alpha h)^n\right]^{-m}$$

$$\chi(h) = \left[1 - \ln(h)/\ln(h_m)\right]$$



透水係数

等温透水係数

$$K_{Lh}(h) = K_S S_e^l \left[1 - \left(1 - S_e^{1/m}\right)^m\right]^2$$

非等温透水係数

$$K_{LT}(T) = K_{Lh}(h)\left(hG_{wT}\frac{1}{\gamma_0}\frac{d\gamma}{dT}\right)$$

等温水蒸気拡散係数

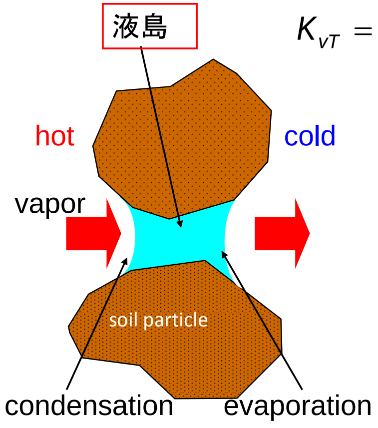
$$K_{vh} = \frac{D}{\rho_w}\rho_{vs}\frac{Mg}{RT}H_r$$

非等温水蒸気拡散係数

$$K_{vT} = \frac{D}{\rho_w}\eta H_r\frac{d\rho_{vs}}{dT}$$

K_s: 飽和透水係数, S_e: 有効飽和度, G_{wT}: 促進係数, γ: 土中水の表面張力, D: 水蒸気拡散係数, ρ_{vs}: 飽和水蒸気密度, M: 水1モルの質量, g: 重力加速度, R: 気体定数, H_r: 相対湿度, η: 水蒸気促進係数

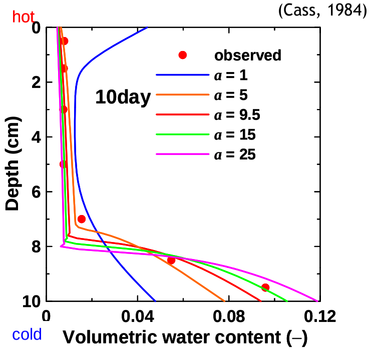
促進係数η



$$K_{vT} = \frac{D}{\rho_w}\eta H_r\frac{d\rho_{vs}}{dT}$$

$$\eta = a + b\frac{\theta}{\theta_s} - (a-1)\exp\left\{-\left[\left(1+\frac{2.6}{\sqrt{f_c}}\right)\frac{\theta}{\theta_s}\right]^4\right\}$$

(Cass, 1984)



演習１　液状水・水蒸気・熱同時移動

この演習では，Nassar and Horton（1992）による，上端と下端を閉じ（ゼロフラックス），ある温度勾配を与えた，シルトロームを充填した10cmカラム内の体積含水率，水分フラックス，温度，濃度変化の計算を行う。

参考文献：Nassar I.N., and R. Horton, Simultaneous transfer of heat, water, and solute in porous media, I. Theoretical development, Soil Science Society of America Journal, 56, 1350-1356, 1992.

Project Manager

Button “New”
Name: Coupled
Description: Coupled Water, Vapor and Heat Transport
Button “OK”
Button “Open”

Main Processes

Heading: Coupled Water, Vapor and Heat Transport
Check Box: Water Flow
Check Box: Vapor Flow
Check Box: Solute Transport
Radio Button: General Solute Transport
Check Box: Heat Transport
Button “Next”

Geometry Information

Length units: cm
Number of Soi1 Materials: 1
Decline from Vertica1 Axes: 0（horizontal flow）
Depth of the Soi1 Profile: 10 cm
Button “Next”

Time Information

Time units: Days
Final Time: 25
Initia1 Time Step: 0.01
Minimum Time Step: 0.00001
Maximum Time Step: 5

Button “Next”

Print Information

Check T-Level Information
Check Screen Output
Check Hit Enter at the End
Number of Print Times: 10
Button “Select Print Times”
Print Times: 0.25 0.5 1 2 3 4 5 10 14 25
Button “OK”
Button “Next”

Water Flow － Iteration Criteria

Water Content Tolerance: 5.e-06
Button “Next”

Water Flow － Soil Hydraulic Model

Keep default values as follows:
Radio button － van Genuchten-Mualem
Radio button － No hysteresis
Button “Next”

Water Flow － Soil Hydraulic Parameters

Residual water content, Qr = 0.03
Saturated water content, Qs = 0.499
Alpha = 0.036
n = 1.56
Ks = 33.7
l = 0.5
Check Box: Temperature Dependence
Button “Next”

Water Flow － Boundary Conditions

Upper Boundary Condition: Constant Flux
Lower Boundary Condition: Constant Flux
Initia1 Conditions: In the Water Content
Button “Next”

Water Flow － Constant Boundary Fluxes

Upper Boundary Flux: 0 (no flux)

Lower Boundary Flux: 0 (no flux)
Initial Condition: in Water Contents
Button “Next”

Solute Transport ― General Information

Leave default values
Button “Next”

Solute Transport ― Solute Transport Parameters

Leave default values for tracer, except
Bulk Density = 1.5 cm^3/g
Disp. = 1 cm
Frac = 1 (fraction of sorption sites at equilibrium with the solution)
ThImob = 0 (immobile water content)
Button “Next”

Solute Transport ― Transport and Reaction Parameters

Leave default values for tracer
Button “Next”

Solute Transport ― Boundary Conditions

Upper Boundary Condition: Concentration Flux BC
Boundary Condition = 0
Lower Boundary Condition: Concentration Flux BC
Boundary Condition = 0
Button “Next”

Heat Transport ― Heat Transport Parameters

Leave default values for loam
Temperature Amplitude: 0
Button “Next”

Heat Transport ― Boundary Conditions

Upper Boundary Condition: Temperature BC
Boundary value = 10 (cold end)
Lower Boundary Condition: Temperature BC
Boundary value = 25 (warm end)
Button “Next”

HYDRUS-ID Guide: Do you want to run Profile Application

Button “OK”

Profile Information － Graphical Editor

Conditions -> *Profile Discretization* (or from the tool bar)

Click the “*Number*” command from the Edit Bar and specify 51 nodes.

Conditions -> *Initial Conditions* -> *Water Content* (or from the tool bar)

Button “Edit condition”

Select with the Mouse the entire soil profile

Specify initial water content of 0.134

Conditions -> *Initial Conditions* -> *Concentration* 1 (or from the tool bar)

Button “Edit condition”

Select with the Mouse the entire soil profile

Specify initial water content of 1

Include observation points at 0, 2, 4, 6, 8, and 10 cm

Save and Exit

Execute HYDRUS-ID

OUTPUT:

Observation Points

Profile Information

Mass Balance Information

演習 2 水蒸気移動と蒸発・凝縮演習

この演習では，宮﨑（1976）による砂質土中内の水蒸気移動の実験を，HYDRUS-1D を使って再現する。周囲を断熱した 10cm の砂カラムに対し，閉じた下端は 20°C に保ち，上端は温度 37°C と湿度 85-90%の空気に開放した。

Program Manager

Button “New”

Name: Condensation

Description: Miyazaki 1976

Button “OK”

Main Processes

Heading: Vapor transport and condensation

Check “Vapor Flow” “Heat Transport”

Button “Next”

Geometry Information

Depth of Soil Profile: 10

Button “Next”

Time Information

Final Time: 30

Initial Time Step: 1e-005

Minimum Time Step: 1e-006

Maximum Time Step: 0.01

Check Time-Variable Boundary Condition

Number of Time-Variable Boundary Records: 30

Button “Next”

Print Information

Number of Print Times: 5

Button “Select Print Times”

Print Times: 5, 10, 16, 21, 30

Button “OK”

Button “Next”

Iteration Criteria

Button “Next”

Soil Hydraulic Model

Check “Dual-porosity (Durner, dual van Genuchten – Mualem)”
Button “Next”

Water Flow Parameters

Residual water content, Qr = 0.001
Saturated water content, Qs = 0.325
Alpha = 0.0655
n = 4.73
Ks = 3456
l = 0.5
w2 = 0.067
Alpha2 = 0.00435
n2 = 1.23
Check “Temperature Dependence”
Button “Next”

Water Flow Boundary Conditions

Upper Boundary Condition: Atmospheric BC with Surface Layer
Lower Boundary Condition: Constant Flux (no flux)
Initial Condition: In Water Contents
Max h at Soil Surface: 0
Button “Next”

Constant Boundary Fluxes

Lower Boundary Flux: 0
Button “Next”

Heat Transport Parameters

Leave default values for Sand
Temperature Amplitude = 0
Button “Next”

Heat Transport Boundary Conditions

Upper Boundary Condition: Temperature BC
Lower Boundary Condition: Temperature BC
Button “Next”

Time Variable Boundary Conditions

Copy the variable boundary conditions from the Excel file

Time	Precip.	Evap.	hCritA	tTop	tBot	Ampl
1	0.0153272	0	10000000	36.3	23.5	0
2	0.0157044	0	10000000	36.3	23.5	0
3	0.0160816	0	10000000	36.3	23.5	0
•	•	•	•	•	•	•
•	•	•	•	•	•	•
•	•	•	•	•	•	•
30	0.026266	0	10000000	36.3	23.5	0

Button “Next”

HYDRUS-1D guide: Do you want to run PROFILE application?

Button “OK”

Profile Information – Graphical Editor

Conditions -> *Initial Conditions* -> *Water Content* (or from the tool bar)

Button “Edit condition”

Select with the Mouse the entire soil profile

Specify initial water content of 0.0045

Include observation points at 0.5, 1.5, 3, 5, 7, 8.5, and 9.5 cm

Save and Exit

Execute HYDRUS-1D

Output:

Observation Points

Profile Information

Mass Balance Information

HP1: A COUPLED NUMERICAL CODE FOR VARIABLY SATURATED WATER FLOW, SOLUTE TRANSPORT, AND BIOGEOCHEMISTRY IN SOIL SYSTEMS

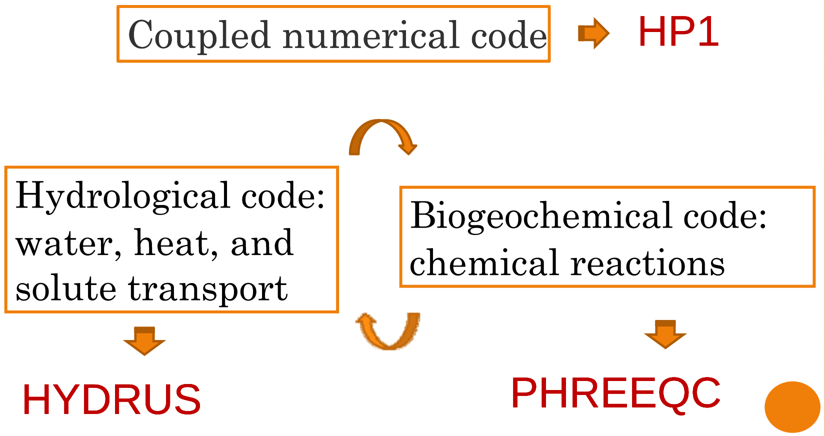
Nobuo Toride, Dimitar Antonov, Daiwen Chen
Mie University

Irrigation & Drainage Society, Soil Physics Meeting
October 19, 2008

OUTLINE

- Introduction: Why Coupled Reactive Transport Models?
- HP1: HYDRUS1D - PHREEQC
- Application of the code

What is a Coupled numerical code for reactive transport modeling?


Coupled numerical code → HP1

Hydrological code: water, heat, and solute transport → HYDRUS

Biogeochemical code: chemical reactions → PHREEQC

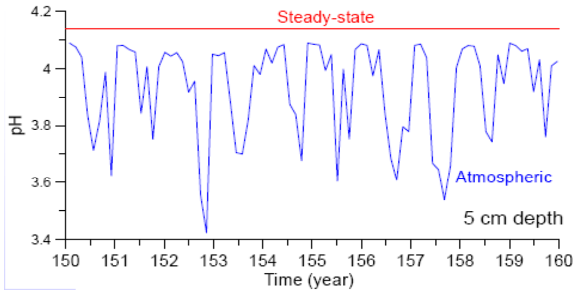
Cycling of major and trace elements in soil-plant systems

- Heterogeneous physical/chemical properties
- Water flow under rainfall – evaporation conditions
- Cation exchange processes
- Surface complexation
- Precipitation/dissolution
- Volatilization
- Root growth and water uptake
- Uptake of metals by plants

Soils are open systems

- Thus: changing geochemical conditions do not only result from static geochemical reactions (“batch”)
- But also: from
  - Amount of available soil water
  - Changing groundwater table
  - Geochemical conditions of water flow

Transient flow conditions ⇒ transient geochemical conditions (*example*)

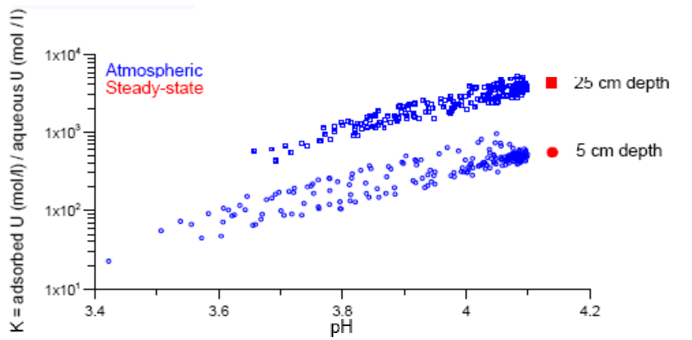


pH variations of soil water under the atmospheric condition:

- *water content variations induce pH variations (dry soil ⇒ low pH)*
- *pH variations ⇒ variations in sorption potential (low pH ⇒ low sorption)*

(from HP1 Training Course handouts. 2006. Mol, Belgium)

pH effects on the distribution coefficient K_d for Uranium adsorption (*example*)



(from HP1 Training Course handouts. 2006. Mol, Belgium)

At least one order of magnitude variation in *K*

Process understanding and assessment of pollutant migration

- Requires a coupled reactive transport model (RTM)
  - Water flow
  - Multicomponent solute transport
  - Biogeochemical processes and reactions (e.g., nitrogen cycle, carbon cycle, etc.)
  - Interaction with biosphere (vegetation), groundwater, surface water (e.g., run off)

What are fully coupled models?

Fully coupled models combain two independent tools:

- Groundwater flow models (e.g. HYDRUS, VS2DI, MODFLOW, etc.)

and

- Chemical reaction models (e.g. PHREEQC, MINTEQA2, EQ3NR, etc.)

Why fully coupled models and not geochemical models?

- Adding diffusive and dispersive transport
- Adding physical /spatial/ heterogeneity (e.g. hydraulic parameters)
- Coupling with time-dependent processes as heat transfer, evolving medium properties
- Providing information on the spatial distribution of variables and processes

Why fully coupled models and not classical hydrological models?

- Adding mechanistic models for sorption and their effect on chemical mobility
- Adding effects of aqueous complexation and new species on chemical mobility
- Conversion of contaminants via biochemical reactions in parallel and sequential reaction networks
- Adding dissolution/precipitation and their effect on adsorption

What is HP 1?

HP 1

A Coupled Numerical Code
(Jacques and Šimůnek, 2005)

- **H**YDRUS-1D

  (Šimůnek et al., 1998):

  Computer program for simulating water, heat and solute movement in one-dimensional variably saturated media.

- **P**HREEQC

  (Parkhurst and Appelo, 1999):

  Computer program for simulating biogeochemical reactions.

HYDRUS-1D features

- Variable saturated water flow
- Solute transport
- Heat transport
- Root water uptake

PHREEQC features

- Aqueous complexation
- Cation exchange
- Surface complexation – diffuse double layer model and non-electrostatic surface complexation model
- Precipitation/dissolution
- Chemical kinetics
- Redox reactions
- Biological reactions

PHREEQC: Fundamentals

PHREEQC is:

A computer program for biogeochemical reactions, based on the *law of mass action*.

Example: For the reaction : $CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$

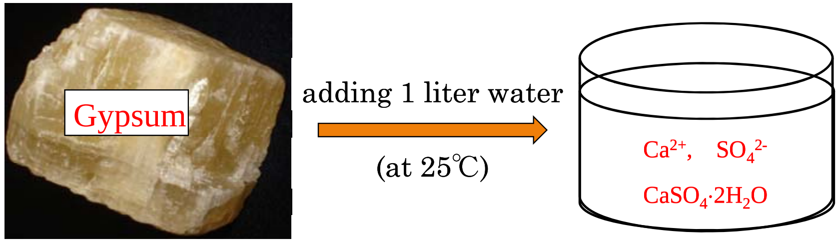
applying *the law of mass action* gives:

$$K = \frac{[Ca^{2+}][SO_4^{2-}][H_2O]^2}{[CaSO_4 \cdot 2H_2O]} = 10^{-4.6}$$

where K is the equilibrium constant and "[ ]" represents concentration

---

PHREEQC Example: Solubility of Gypsum



Q1: If the solution is at saturated state, what is the concentration of SO_4^{2-} (or Ca^{2+}) in the liquid phase?

Q2: If 0.001 mol $CaCl_2$ is added to the saturated solution, what is the SO_4^{2-} concentration in equilibrium?

Q3: If repeat the addition of 0.001mol $CaCl_2$ 10 times, what will be the equilibrium SO_4^{2-} concentration?

Results

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

Low solubility of gypsum leads to the solubility product as

$$K = \frac{\left[Ca^{2+}\right]\left[SO_4^{2-}\right][H_2O]^2}{[CaSO_4 \cdot 2H_2O]} = 10^{-4.6} \quad \Rightarrow \quad K = \left[Ca^{2+}\right]\left[SO_4^{2-}\right] = 10^{-4.6}$$

Q1: Substituting $\left[SO_4^{2-}\right] = \left[Ca^{2+}\right]$ into the solubility product results in:

$$K = \left[Ca^{2+}\right]\left[SO_4^{2-}\right] = \left[SO_4^{2-}\right]^2 = 10^{-4.6} \quad \Rightarrow \quad \left[SO_4^{2-}\right] = 0.00501 \ \ (mol/l)$$

Results

Q2: Same amount of Δx for Ca^{2+} and SO_4^{2-} precipitates at the new equilibrium. Hence the new concentrations can be given as

$[Ca^{2+}]$ =(0.00501+0.001 - Δx) mol/l, and [SO_4^{2-}] =(0.00501 - Δx) mol/l

Substituting these concentration into the solubility product leads to

$$K = \left[Ca^{2+}\right]_{n-e}\left[SO_4^{2-}\right]_{n-e} = (0.00601 - \Delta x)(0.00501 - \Delta x) = 10^{-4.6}$$

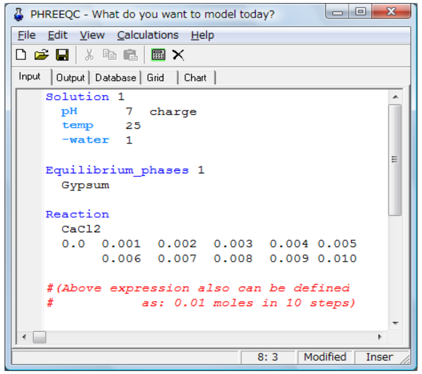
$$\Rightarrow \quad \Delta x = 0.00048 \quad (mol/l)$$

$$\left[Ca^{2+}\right]_{n-e} = 0.00601 - \Delta x = 0.00553 \quad (mol/l)$$

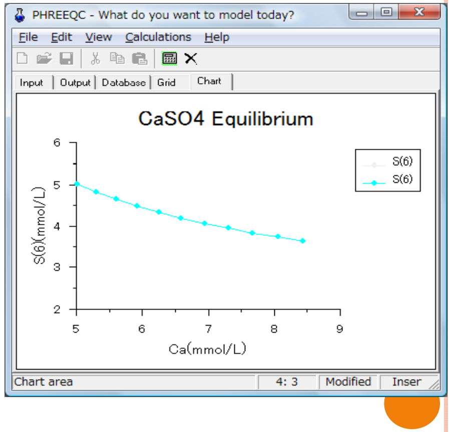
$$\left[SO_4^{2-}\right]_{n-e} = 0.00501 - \Delta x = 0.00453 \quad (mol/l)$$

Results

Q 3: Using the PHREEQC code.



```
Solution 1
  pH      7   charge
  temp    25
  -water  1

Equilibrium_phases 1
  Gypsum

Reaction
  CaCl2
  0.0   0.001  0.002  0.003  0.004 0.005
        0.006  0.007  0.008  0.009 0.010

#(Above expression also can be defined
#            as: 0.01 moles in 10 steps)
```



PHREEQC: General description

PHREEQC can simulate:

(*i*) equilibrium reactions

- aqueous complexation (reactions in pore-water)
- cation exchange (on clay, organic matter, etc.)
- surface complexation (e.g. iron oxyhydroxides)
- mineral dissolution/precipitation, etc.

PHREEQC: General description

Example equilibrium reaction

Na^+ - Ca^{2+} cation exchange process:

$$Na^+ + 1/2Ca\text{-}X_2 \leftrightarrow Na\text{-}X + 1/2Ca^{2+}$$

where X^- represents the amount of exchange sites [mol/kg soil]

and the *law of mass action* gives:

$$K_{Na/Ca} = \frac{[Na\text{-}X][1/2Ca^{2+}]}{[Na^+][1/2Ca\text{-}X_2]}$$

where $K_{Na/Ca}$ is the equilibrium constant and “[ ]“ represents concentration

PHREEQC: General description

PHREEQC can simulate:

(*ii*) kinetic reactions

- degradation reactions (e.g., nigrogen cycle: Org-N→NH_4^+→NO_3^- →N_2)
- oxidation-reduction reactions (e.g., pyrite (FeS_2) oxidation)

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

- radioactive decay (uranium-238 chain: U-238→U-234→Th-230→Ra-226)

PHREEQC: General description

Example kinetic reaction

Nitrogen transformation process:

Fertilizer Org_N → Ammonium NH_4^+ → Nitrate NO_3^- → Nitrogen gas N_2

with the first-order rate degradation reactions:

$$\frac{d\text{Org-N}}{dt} = -\mu_{Org-N}\text{Org-N} \qquad \frac{dNH_4^+}{dt} = -\mu_{NH_4^+}NH_4^+ + \mu_{Org-N}\text{Org-N} \qquad \frac{dNO_3^-}{dt} = -\mu_{NO_3^-}NO_3^- + \mu_{NH_4^+}NH_4^+$$

where $\mu_{Org\text{-}N}$, μ_{NH_4}, *and* μ_{NO_3} are the first-order rate constants.

- In PHREEQC, the rate constant μ could be function of the temperature.

PHREEQC: General description

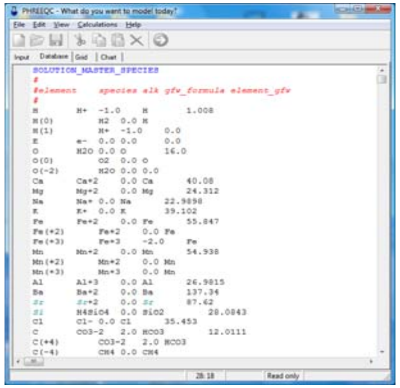
PHREEQC can simulate:

(*iii*) mixed equilibrium/kinetic reactions

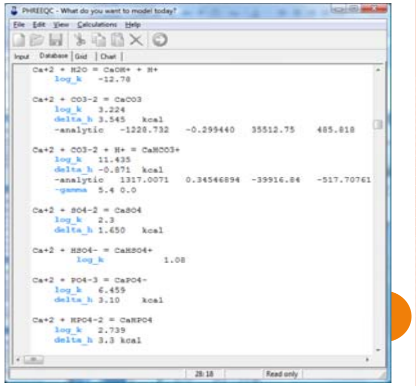
- chain reactions (modeled as kinetic type) including adsorbed phase (modeled as equilibrium type), etc.

PHREEQC: General description

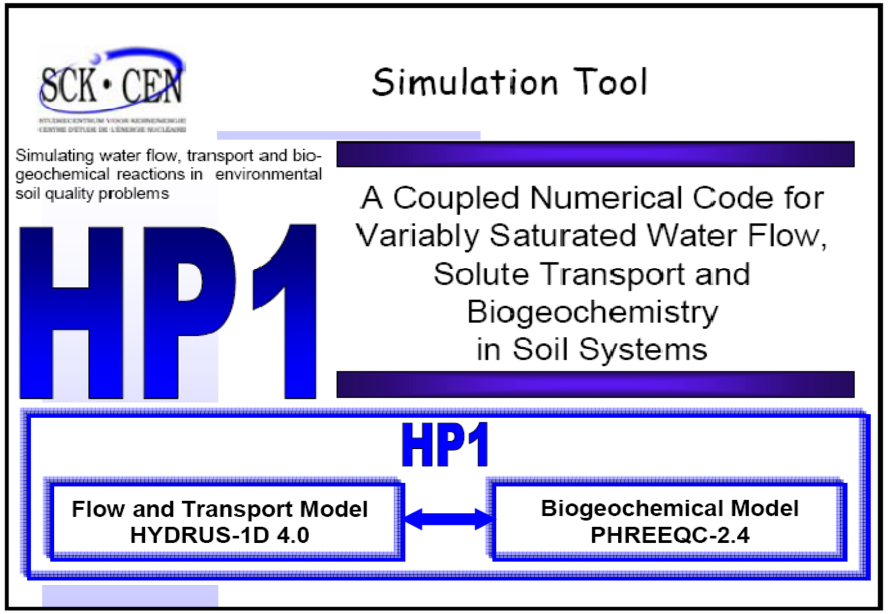
PHREEQC contains databases with chemical definitions (*species, complexes, mineral solubility, etc.*) and constants needed to do the calculations.



```
SOLUTION_MASTER_SPECIES
#
#element     species alk gfw_formula element_gfw
#
H         H+   -1.0     H         1.008
H(0)           H2   0.0 H
H(1)           H+   -1.0     0.0
E         e-   0.0 0.0       0.0
O         H2O 0.0 O          16.0
O(0)           O2   0.0 O
O(-2)          H2O 0.0 0.0
Ca        Ca+2      0.0 Ca        40.08
Mg        Mg+2      0.0 Mg        24.312
Na        Na+ 0.0 Na         22.9898
K         K+   0.0 K         39.102
Fe        Fe+2      0.0 Fe        55.847
Fe(+2)         Fe+2      0.0 Fe
Fe(+3)         Fe+3      -2.0      Fe
Mn        Mn+2      0.0 Mn        54.938
Mn(+2)         Mn+2      0.0 Mn
Mn(+3)         Mn+3      0.0 Mn
Al        Al+3      0.0 Al        26.9815
Ba        Ba+2      0.0 Ba        137.34
Sr        Sr+2      0.0 Sr        87.62
Si        H4SiO4    0.0 SiO2           28.0843
Cl        Cl- 0.0 Cl         35.453
C         CO3-2     2.0 HCO3           12.0111
C(+4)          CO3-2     2.0 HCO3
C(-4)          CH4 0.0 CH4
```



```
Ca+2 + H2O = CaOH+ + H+
     log_k    -12.78

Ca+2 + CO3-2 = CaCO3
     log_k    3.224
     delta_h 3.545    kcal
     -analytic    -1228.732    -0.299440    35512.75    485.818

Ca+2 + CO3-2 + H+ = CaHCO3+
     log_k    11.435
     delta_h -0.871  kcal
     -analytic    1317.0071    0.34546894    -39916.84    -517.70761
     -gamma   5.4 0.0

Ca+2 + SO4-2 = CaSO4
     log_k    2.3
     delta_h 1.650    kcal

Ca+2 + HSO4- = CaHSO4+
          log_k             1.08

Ca+2 + PO4-3 = CaPO4-
     log_k    6.459
     delta_h 3.10     kcal

Ca+2 + HPO4-2 = CaHPO4
     log_k    2.739
     delta_h 3.3 kcal
```



SCK•CEN

STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE

Simulation Tool

Simulating water flow, transport and bio-geochemical reactions in environmental soil quality problems

HP1

A Coupled Numerical Code for Variably Saturated Water Flow, Solute Transport and Biogeochemistry in Soil Systems

The convection–dispersion equation (CDE) in HP1

The general solute transport equation in HP1 is:

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

where

- i (= 1,…N_m) is the aqueous species number (N_m is the total number of aqueous species),
- $c_{l,i}$: aqueous concentration phase [ML^{-3}],
- θ : volumetric water content [L^3L^{-3}],
- D^w : diffusion-dispersion coefficient [L^2T^{-1}],
- q : water flux [LT^{-1}],
- S : water uptake term [$L^3L^{-3}T^{-1}$],
- $c_{r,i}$: the concentration of the sink term [ML^{-3}], and
- $\boldsymbol{R_i}$: general source/sink term due to geochemical reactions [$ML^{-3}T^{-1}$].

Source/Sink Term R_i

The general source/sink term R_i represents any change of the soil system due to the biogeochemical processes, and namely:

- equilibrium homogeneous and heterogeneous reactions,
- kinetic homogeneous and heterogeneous reactions,
- mixed equilibrium - kinetic reactions.

HP1 coupling procedure

- Coupling method: non-iterative sequential approach (weak coupling)
- Within a single time step:
  - Solve water flow equation (HYDRUS)
  - Solve heat transport equation (HYDRUS)
  - Solve CDE for solute transport like inert components (HYDRUS)
  - Calculate speciations, equilibrium reactions, kinetic reactions, etc. … for each cell (PHREEQC)

HP1 coupling procedure

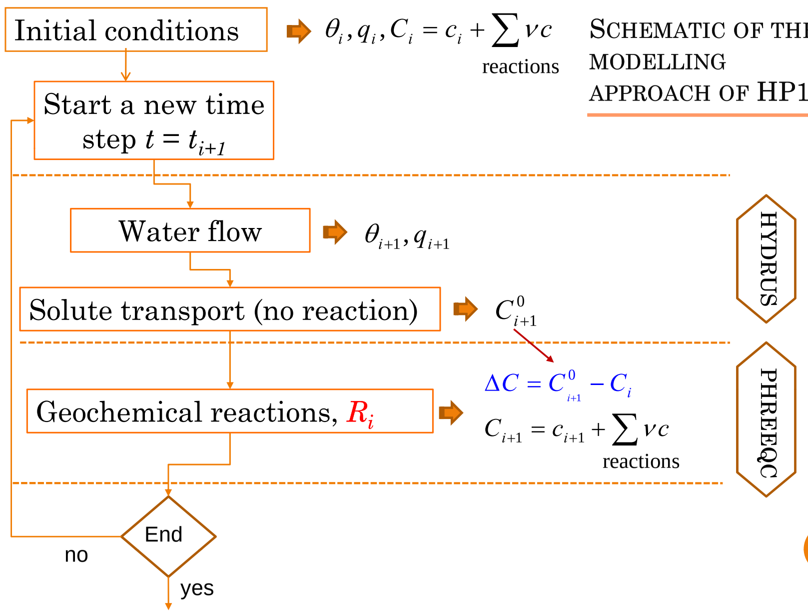
$$\frac{\partial \theta c_{l,i}}{\partial t} = \frac{\partial}{\partial x}\left(\theta D^{w} \frac{\partial c_{l,i}}{\partial x}\right) - q\frac{\partial c_{l,i}}{\partial x} - Sc_{r,i} + R_i$$

First

HYDRUS-1D
(physical transport part)

Second

PHREEQC
(geochemical reactions part)



$\theta_i, q_i, C_i = c_i + \sum_{\text{reactions}} \nu c$

θ_{i+1}, q_{i+1}

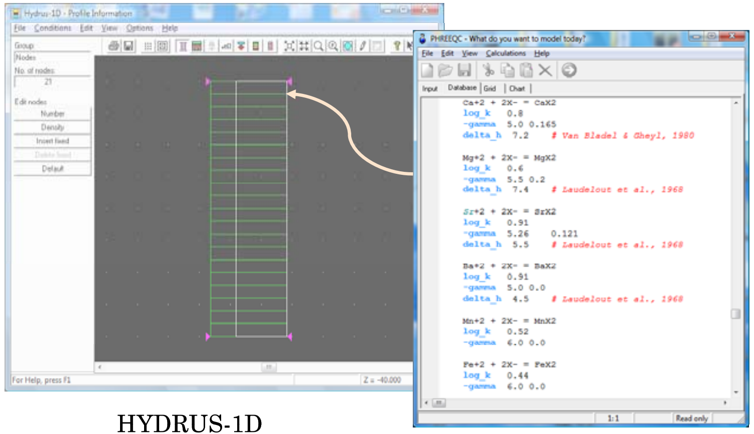
C^0_{i+1}

$\Delta C = C^0_{i+1} - C_i$

$C_{i+1} = c_{i+1} + \sum_{\text{reactions}} \nu c$

SCHEMATIC OF THE MODELLING APPROACH OF HP1

HP1 coupling procedure



```
Ca+2 + 2X- = CaX2
log_k   0.8
-gamma  5.0 0.165
delta_h  7.2     # Van Bladel & Gheyl, 1980

Mg+2 + 2X- = MgX2
log_k   0.6
-gamma  5.5 0.2
delta_h  7.4     # Laudelout et al., 1968

Sr+2 + 2X- = SrX2
log_k   0.91
-gamma  5.26    0.121
delta_h  5.5     # Laudelout et al., 1968

Ba+2 + 2X- = BaX2
log_k   0.91
-gamma  5.0 0.0
delta_h  4.5     # Laudelout et al., 1968

Mn+2 + 2X- = MnX2
log_k   0.52
-gamma  6.0 0.0

Fe+2 + 2X- = FeX2
log_k   0.44
-gamma  6.0 0.0
```

HYDRUS-1D
(nonreactive solute transport in the profile)

At each node, PHREEQC evaluates chemical reactions.

HP1 coupling procedure

- The total mass balance for the geochemical reactions at each node is considered in the PHREEQC module
- Since explicit time scheme is used, small Δt is necessary
- The coupling procedure is inefficient and time-consuming

Application of the code

- Transport of heavy metals (Zn^{2+}, Pb^{2+}, and Cd^{2+}) subject to multiple cation exchange
- Transport with mineral dissolution of amorphous SiO_2 and gibbsite ($Al(OH)_3$)
- Heavy metal transport in a soil with a pH-dependent cation exchange complex

---

Application of the code

- Infiltration of a hyperalkaline solution in a clay sample including kinetic precipitation-dissolution of kaolinite, illite, quartz, calcite, dolomite, gypsum, hydrotalcite, and sepiolite
- Long-term transient flow and transport of major cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) and heavy metals (Cd^{2+}, Zn^{2+}, and Pb^{2+}) in a soil profile
- Kinetic biodegradation of NTA /nitrilotriacetate/ (biomass, cobalt)

Application of the code

- Transport of TNT /trinitrotoluene; trotyl/ and its daughter products
- Uranium transport in agricultural field soil (example considers surface complexation reactions due to Fe-oxides)
- Horizontal infiltration and adsorption of piggery enfluent

HP1 summary

- Tool that integrates physical – chemical – biological aspects of chemical migration in soils
- Multiple biogeochemical reactions
- Complex flow fields
- Spatial variability

HP1 summary

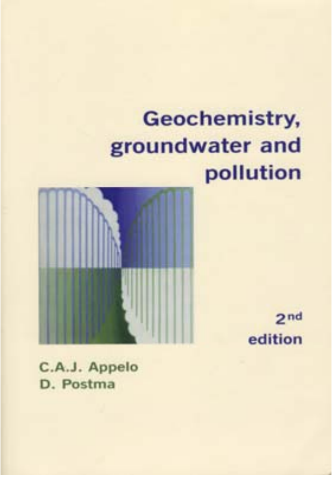
- Interpretation of laboratory and field data
- Tool for understanding qualitatively and quantitatively trends in data
- Sensitivity analyses
- Permits systematic evaluation of impact of initial and boundary conditions on model output

Literature

- Jacques, D., and J. Šimunek. 2005. User Manual of the Multicomponent Variably-Saturated Flow and Transport Model HP1: Description, Verification, and Examples. Version 1.0. BLG-998. Waste and Disposal, SCK•CEN, Mol, Belgium, 79 pp.
- Jacques, D., J. Šimunek, D. Mallants, and M. Th. Van Genuchten. 2006. Operator-splitting errors in coupled reactive transport codes for transient variably saturated flow and contaminant transport in layered soil profiles. *J. Contam. Hydrology, 88*, 197-218.
- Jacques, D., J. Šimunek, D. Mallants, and M. Th. Van Genuchten. 2008. Modelling coupled water flow, solute transport and geochemical reactions affecting heavy metal migration in a podzol soil. *Geoderma, 145,* 449–461.

Literature

- Appelo, C.A.J., and D. Postma. 2005. Geochemistry, groundwater and pollution. Second edition. Balkema Publ., ISBN 04 1536 4280, 649 pp.



Nitrogen transport 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

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

- General Information:
  - Steady-state water flow (q = 1 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)
  - Component Cont with inflow concentration 0.01 mol/l
  - Adsorption description: Freundlich type linear adsorption with distribution coefficient K_d = 5 cm^3/g

Example 1. STADS

- General governing transport equation for linearly adsorbing chemicals (with no degradation) is:

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

where R is the retardation factor equal to: $R=1+\frac{\rho_b K_d}{\theta}$

and K_d is the distribution coefficient [L^3M^{-1}], equal to:

$$c_a=K_d c_l$$

Example 1. STADS

- The general governing transport equation in HP1 is:

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

where R_i represents the source/sink due to geochemical reactions

=> The transport equation for adsorbing chemical is:

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

where considering Freundlich type linear adsorption: $c_a = K_d c_l$

Example 1. STADS

- Modeling linear adsorption in PHREEQC :

Surface complexation reaction:

Sor + Cont = SorCont

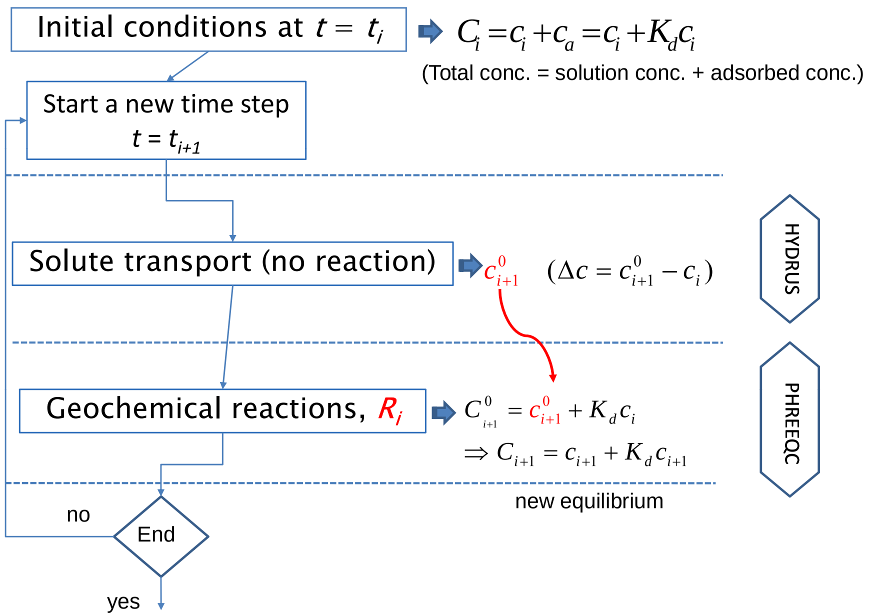
where Sor is the adsorptive surface and SorCont is the adsorbed component.

Applying *the law of mass action* assuming [Sor] is very large (= 1E+100 [mol/l]) gives:

$$K = \frac{[\mathrm{SorCont}]}{[\mathrm{Sor}][\mathrm{Cont}]} = \frac{c_a}{[\mathrm{Sor}]c_l} = \frac{K_d \rho_b c_l}{[\mathrm{Sor}]c_l} = \frac{K_d \rho_b}{[\mathrm{Sor}]} = 10^{2.3}$$

since c_a is small, [Sor] remains almost constant regardless of c_a.

$$c_a = K[\mathrm{Sor}]c_l \approx K_d \rho_b c_l$$



Initial conditions at $t = t_i$ ➡ $C_i = c_i + c_a = c_i + K_d c_i$

(Total conc. = solution conc. + adsorbed conc.)

Start a new time step $t = t_{i+1}$

Solute transport (no reaction) ➡ c_{i+1}^0 $(\Delta c = c_{i+1}^0 - c_i)$

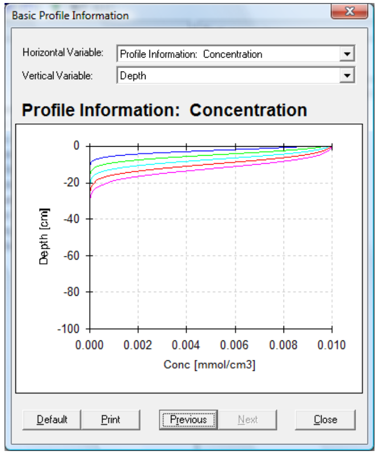
Geochemical reactions, R_i ➡ $C_{i+1}^0 = c_{i+1}^0 + K_d c_i$

$\Rightarrow C_{i+1} = c_{i+1} + K_d c_{i+1}$

new equilibrium

Example 1. STADS

- *Results*



These graphs show the *Cont* concentration distribution through the profile at the initial plus at the printed time steps (four in the example). At the last time step (100 d, the light red graph) the concentration through the whole profile is equal to zero at the 30 cm.

Example 1. Highlights

Input data: HYDRUS-1D

- Transport solver (HYDRUS-1D)
- Using the graphical interface
- No solute reaction parameters defined in HYDRUS-1D!

  To be defined in HYDRUS-1D:
  - Water flow, solute physical transport parameters
  - Profile discretization, physical heterogeneity
  - Initial conditions for water transport
  - Boundary conditions

Example 1. Highlights

Input data: PHREEQC

- Chemical solver (PHREEQC)
  - Xxxxxx.xxx (database) (e.g., *phreeqc.dat*, *phreeqcU.dat*, *minteq.dat*)
  - Phreeqc.in
- Using the graphical interface

  To be defined in PHREEQC:
  - Initial composition of the solutions (for each cell)
  - If concentration of a master species is zero, a small value should be defined (e.g., 10^{-20} mol / l)
  - Geochemical reactions (exchange, equilibrium phases, kinetics)
  - Chemical heterogeneity
  - Keyword “TRANSPORT” with the number of cells

Example 1. Highlights

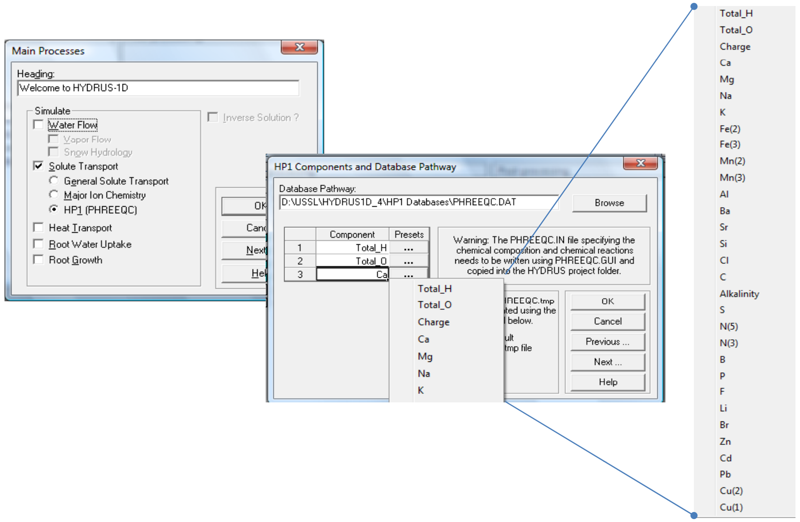
Input data: HP1

- HP1
  - Species.in
- By defining:
  - The location of the database, e.g.

    D:¥USSL¥HYDRUS1D_4¥HP1Databases¥PHREEQC.DAT
  - A list of primary (master) species, e.g.:
    - Na
    - Cl

    or
    - Cont

Example 1. Highlights



Main Processes

Heading: Welcome to HYDRUS-1D

Simulate

☐ Water Flow

☐ Vapor Flow

☐ Snow Hydrology

☑ Solute Transport

○ General Solute Transport

○ Major Ion Chemistry

● HP1 (PHREEQC)

☐ Heat Transport

☐ Root Water Uptake

☐ Root Growth

☐ Inverse Solution ?

HP1 Components and Database Pathway

Database Pathway: D:\USSL\HYDRUS1D_4\HP1 Databases\PHREEQC.DAT

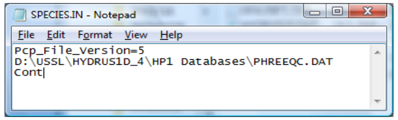
	Component	Presets
1	Total_H	...
2	Total_O	...
3	Ca	...

Warning: The PHREEQC.IN file specifying the chemical composition and chemical reactions needs to be written using PHREEQC.GUI and copied into the HYDRUS project folder.

Example 1. Highlights

Defining new element /not in the database/ (e.g., Cont)

- open the example folder (e.g.,
  D:¥USSL¥HYDRUD1D_4¥Projects¥Direct)
- open the “SPECIES.IN” file (e.g., Notepad etc.)
- enter the new element Cont as shown below:



```
Pcp_File_Version=5
D:\USSL\HYDRUS1D_4\HP1 Databases\PHREEQC.DAT
Cont
```

- close the HYDRUS-1D window and re-open it

Example 2. CATEX

- General Information:
  - Steady-state water flow (q = 1 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-potassium-chloride*) initial solution
  - Cation exchange capacity CEC = 0.73 mmol/kg soil
  - CaCl$_2$ (*calcium chloride*) solution with inflow concentration 0.0006 mol/l

Example 2. CATEX

- Governing transport equations:

$$\frac{\partial C_{l,Ca}}{\partial t} = \frac{\partial}{\partial x}\left(D^w_{Ca}\frac{\partial C_{l,Ca}}{\partial x}\right) - \frac{q}{\theta}\frac{\partial C_{l,Ca}}{\partial x} + R_{Ca} \qquad \frac{\partial C_{l,Cl}}{\partial t} = \frac{\partial}{\partial x}\left(D^w_{Cl}\frac{\partial C_{l,Cl}}{\partial x}\right) - \frac{q}{\theta}\frac{\partial C_{l,Cl}}{\partial x} + R_{Cl}$$

$$\frac{\partial C_{l,Na}}{\partial t} = \frac{\partial}{\partial x}\left(D^w_{Na}\frac{\partial C_{l,Na}}{\partial x}\right) - \frac{q}{\theta}\frac{\partial C_{l,Na}}{\partial x} + R_{Na} \qquad \frac{\partial C_{l,K}}{\partial t} = \frac{\partial}{\partial x}\left(D^w_{K}\frac{\partial C_{l,K}}{\partial x}\right) - \frac{q}{\theta}\frac{\partial C_{l,K}}{\partial x} + R_{K}$$

where R_{Ca}, R_{Cl}, R_{Na} and R_K represent the specific sink term due to the cation exchange interactions

Example 2. CATEX

- Cation exchange equations:

(*i*) 0.5Ca^{2+} +Na-X ↔ 0.5Ca-X$_2$ + Na$^+$

with equilibrium constant: $K_{Ca/Na} = \frac{[CaX\,2]^{0.5}[Na^+]}{[NaX][Ca^{2+}]^{0.5}}$

(*ii*) 0.5Ca^{2+} +K-X ↔ 0.5Ca-X$_2$ + K$^+$

with equilibrium constant: $K_{Ca/K} = \frac{[CaX\,2]^{0.5}[K^+]}{[KX][Ca^{2+}]^{0.5}}$

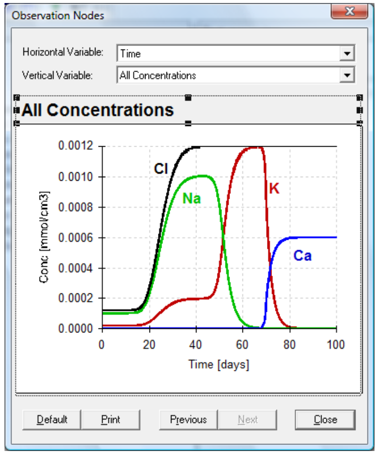
(*iii*) K$^+$ + Na-X ↔ K-X + Na$^+$

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

where **X** represents the amount of the exchange sites (equal to CEC)

Example 2. CATEX

- *Results*



Observation Nodes

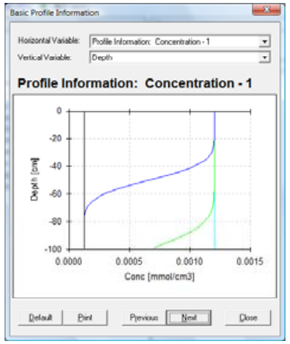
Horizontal Variable: Time

Vertical Variable: All Concentrations

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

Example 2. CATEX

- *Results*

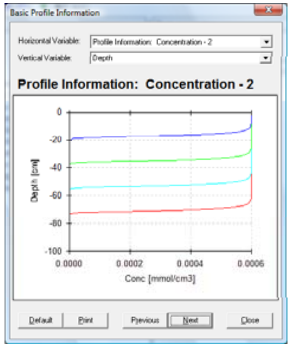


Basic Profile Information

Horizontal Variable: Profile Information: Concentration - 1

Vertical Variable: Depth

The Cl$^-$ concentration in the solute phase through the profile.



Basic Profile Information

Horizontal Variable: Profile Information: Concentration - 2

Vertical Variable: Depth

The Ca^{2+} concentration in the solute phase through the profile.

Example 3. DEGRAD

- General Information:
- Steady-state water flow (*q* = 1 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)
- Component *Conta* undergoing first-order degradation with inflow concentration 0.01 mol/l
- Component *Conta* transfers to component *Contb*, and *Contb* to *Contc*
- Adsorption description: Freundlich type linear adsorption

Example 3. DEGRAD

- The processes scheme for first-order decay chain of linearly adsorbed contaminants *Conta*, *Contb and Contc*:

$$\begin{tikzcd}
Conta \arrow[r, "decay", "\mu_{w,1}"'] \arrow[d, "K_{d,1}"] & Contb \arrow[r, "decay", "\mu_{w,2}"'] \arrow[d, "K_{d,2}"] & Contc \arrow[r, "decay", "\mu_{w,3}"'] \arrow[d, "K_{d,3}"] & {} \\
SorConta \arrow[ur, "decay", "\mu_{s,1}"'] & SorContb \arrow[ur, "decay", "\mu_{s,2}"'] & SorContc \arrow[ur, "decay", "\mu_{s,3}"'] &
\end{tikzcd}$$

Example 3. DEGRAD

- First-order degradation rate equations:

$$\frac{dConta}{dt} = -\mu_{Conta} Conta$$

$$\frac{dContb}{dt} = -\mu_{Contb} Contb$$

$$\frac{dContc}{dt} = -\mu_{Contc} Contc$$

where μ_i is the first-order degradation constant for the i^{th} component [T^{-1}]

Example 3. DEGRAD

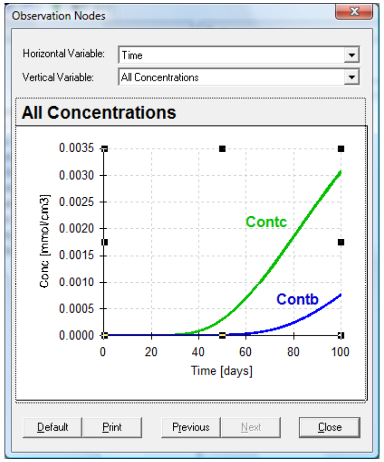
- Modeling first-order degradation rate in PHREEQC :
  - **RATES (# keyword data block)**
    - Contadegradation
    - -start
    - 10 rem parm(1) first-order degradation coefficient (d-1)
    - 20 rate=parm(1)*tot("water")*mol("Conta")
    - 30 moles=-rate*time
    - 40 save moles
    - -end

Example 3. DEGRAD

- Modeling first-order degradation rate in PHREEQC :
  - **KINETICS 1-101 (# keyword data block)**
    - Contadegradation
    - -formula Conta 1.0 Contb -1.0
    - -parms 0.02

Example 3. DEGRAD

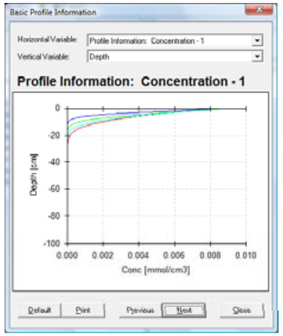
- *Results*



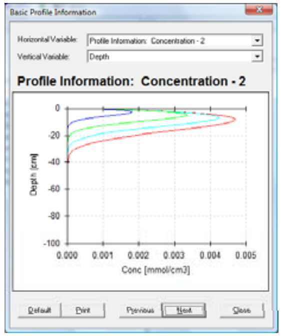
These graphs show the *components* concentration according to the time at the observation point 1 (25 cm of the profile). At the end of the simulation period the second degradation daughter product has the biggest impact.

Example 3. DEGRAD

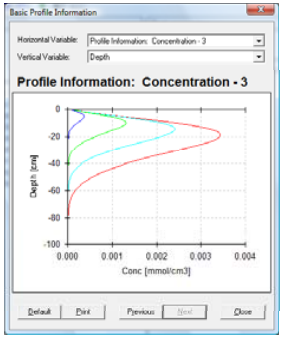
- *Results*


Basic Profile Information
Horizontal Variable: Profile Information: Concentration - 1
Vertical Variable: Depth
Profile Information: Concentration - 1

The *Conta* concentration through the profile


Basic Profile Information
Horizontal Variable: Profile Information: Concentration - 2
Vertical Variable: Depth
Profile Information: Concentration - 2

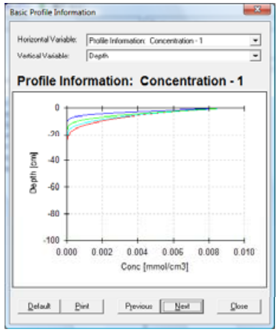
The *Contb* concentration through the profile


Basic Profile Information
Horizontal Variable: Profile Information: Concentration - 3
Vertical Variable: Depth
Profile Information: Concentration - 3

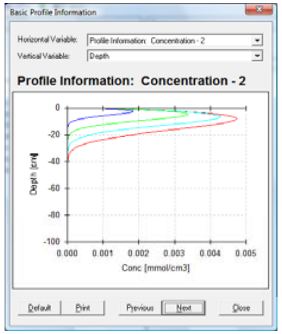
The *Contc* concentration through the profile

Example 3. DEGRAD

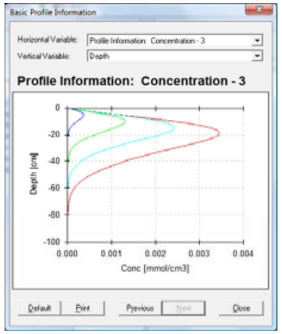
- *Results from HYDRUS-1D simulations:*


Basic Profile Information
Horizontal Variable: Profile Information: Concentration - 1
Vertical Variable: Depth
Profile Information: Concentration - 1

The *Conta* concentration through the profile (HYDRUS-1D)


Basic Profile Information
Horizontal Variable: Profile Information: Concentration - 2
Vertical Variable: Depth
Profile Information: Concentration - 2

The *Contb* concentration through the profile (HYDRUS-1D)


Basic Profile Information
Horizontal Variable: Profile Information: Concentration - 3
Vertical Variable: Depth
Profile Information: Concentration - 3

The *Contc* concentration through the profile (HYDRUS-1D)

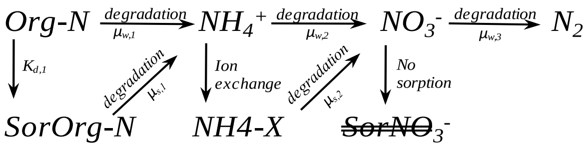
Example 4. NITROG

- General Information:
- Steady-state water flow ($q = 1$ 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-potassium-chloride*) initial solution
- Cation exchange capacity CEC = 0.67 mmol/kg soil
- Organic nitrogen inflow solution with concentration 0.001 mol/l

---

Example 4. NITROG

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



$$\begin{tikzcd}
Org\text{-}N \arrow[r, "degradation", "\mu_{w,1}"'] \arrow[d, "K_{d,1}"] & NH_4^+ \arrow[r, "degradation", "\mu_{w,2}"'] \arrow[d, "Ion\ exchange"] & NO_3^- \arrow[r, "degradation", "\mu_{w,3}"'] \arrow[d, "No\ sorption"] & N_2 \\
SorOrg\text{-}N \arrow[ur, "degradation", "\mu_{s,1}"'] & NH4\text{-}X \arrow[ur, "degradation", "\mu_{s,2}"'] & \cancel{SorNO_3^-} &
\end{tikzcd}$$

Example 4. NITROG

- First-order rate equations:

$$\frac{d\text{Org-N}}{dt} = -\mu_{Org-N}\,\text{Org-N}$$

$$\frac{d\text{NH}_4^+}{dt} = -\mu_{NH_4^+}\,\text{NH}_4^+ + \mu_{Org-N}\,\text{Org-N}$$

$$\frac{d\text{NO}_3^-}{dt} = -\mu_{NO_3^-}\,\text{NO}_3^- + \mu_{NH_4^-}\,\text{NH}_4^+$$

Example 4. NITROG

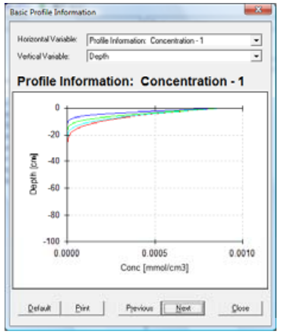
- Cation exchange equation(s):

$$\text{nNH}_4^+ + \text{Cation-X}_n = \text{nNH4-X} + \text{Cation}^{n+}$$

with equilibrium constant: $K_{NH4/Cation} = \frac{[\text{NH4-X}]^n[\text{Cation}^{n+}]}{[\text{Cation-X}_n][\text{NH4}^+]^n}$

Example 4. NITROG

- *Results*

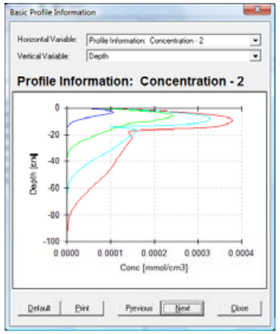

Basic Profile Information

Horizontal Variable: Profile Information: Concentration - 1

Vertical Variable: Depth

Profile Information: Concentration - 1

The *Org-N* concentration in the solute phase through the profile

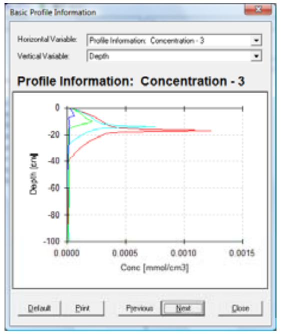

Basic Profile Information

Horizontal Variable: Profile Information: Concentration - 2

Vertical Variable: Depth

Profile Information: Concentration - 2

The ammonium ion concentration in the solute phase through the profile


Basic Profile Information

Horizontal Variable: Profile Information: Concentration - 3

Vertical Variable: Depth

Profile Information: Concentration - 3

The nitrate concentration in the solute phase through the profile

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/cm^3 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/cm^3). Solute dispersivity is 1 cm, assuming no molecular diffusion. The distribution coefficient for linear adsorption K_d is 5 cm^3/g.

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

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

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^{3}L^{-3}], q is the water flux [LT^{-1}] and D_i^w is the dispersion coefficient for the i^{th} species (L^{2}T^{-1}).

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

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

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^{-3}T^{-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:

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

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 [L^3M^{-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:

$$C_{a,i}^{W} = K_d \rho_b C_{l,i} = K_d^W C_{l,i} \tag{5}$$

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

$$Sor + Cont = SorCont \tag{6}$$

$$K_d^w = \frac{[SorCont]}{[Sor][Cont]} \qquad [SorCont] = K_d^w [Sor][Cont] \tag{7}$$

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

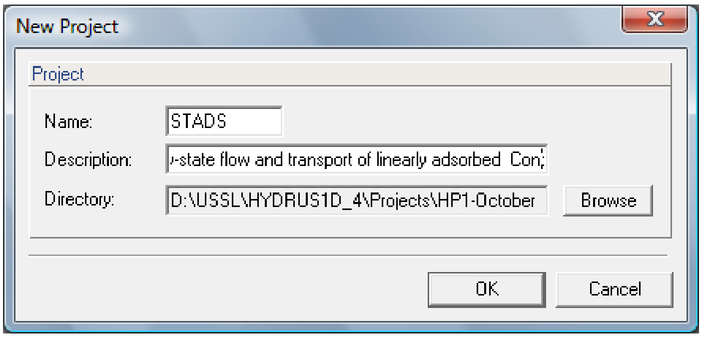
$$K_d^w = \frac{K_d \rho_b}{[Sor]} \tag{8}$$

In this example, assuming [*Sor*]= 1E+100 [mol/l] with $K_d = 5$ [cm^3/g] and $\rho_b = 1.5$ [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***



Name: STADS

Description: ,-state flow and transport of linearly adsorbed Con;

Directory: D:\USSL\HYDRUS1D_4\Projects\HP1-October

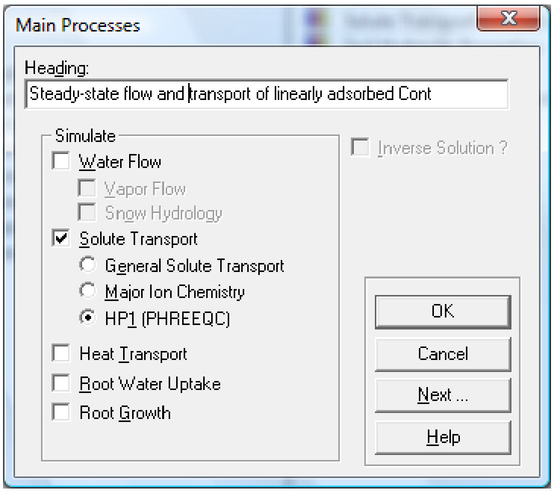
Name: STADS

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!

Main Processes



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

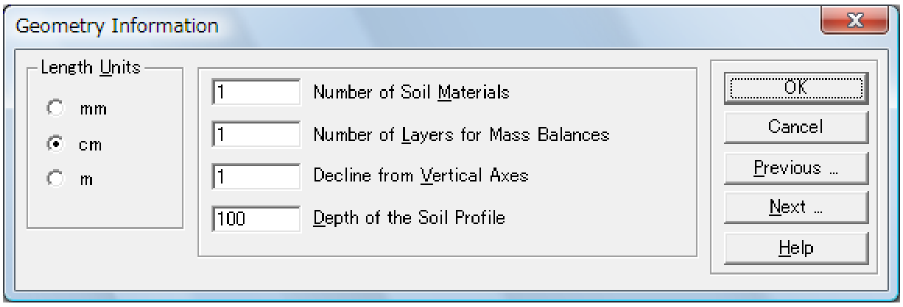
Simulate
☐ Water Flow
☐ Vapor Flow
☐ Snow Hydrology
☑ Solute Transport
○ General Solute Transport
○ Major Ion Chemistry
● HP1 (PHREEQC)
☐ Heat Transport
☐ Root Water Uptake
☐ Root Growth

☐ Inverse Solution ?

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

Simulate: Solute Transport and check "HP1 (PHREEQC)" option.

Geometry Information



Length Units
○ mm
● cm
○ m

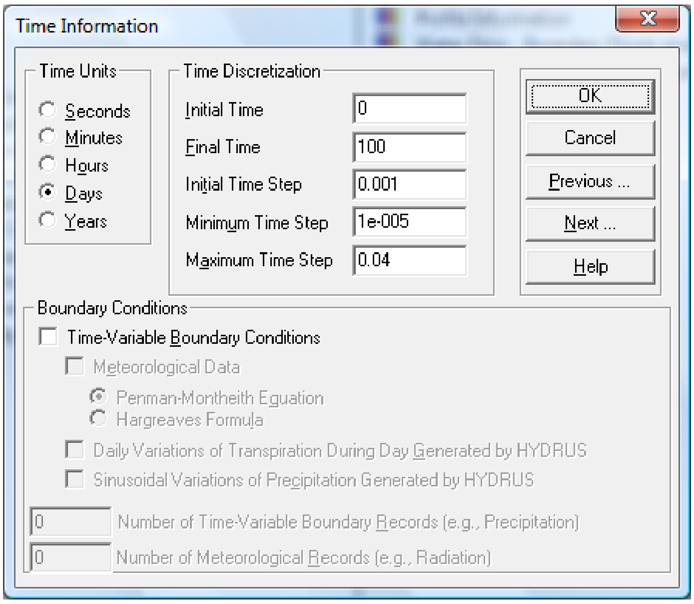
1 Number of Soil Materials
1 Number of Layers for Mass Balances
1 Decline from Vertical Axes
100 Depth of the Soil Profile

Length Units: cm

Depth of the Soil Profile: 100 cm

Button: "Next"

Time Information



Time Information

Time Units

○ Seconds
○ Minutes
○ Hours
● Days
○ Years

Time Discretization

Initial Time: 0
Final Time: 100
Initial Time Step: 0.001
Minimum Time Step: 1e-005
Maximum Time Step: 0.04

Boundary Conditions

☐ Time-Variable Boundary Conditions
☐ Meteorological Data
● Penman-Montheith Equation
○ Hargreaves Formula
☐ Daily Variations of Transpiration During Day Generated by HYDRUS
☐ Sinusoidal Variations of Precipitation Generated by HYDRUS
0 Number of Time-Variable Boundary Records (e.g., Precipitation)
0 Number of Meteorological Records (e.g., Radiation)

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

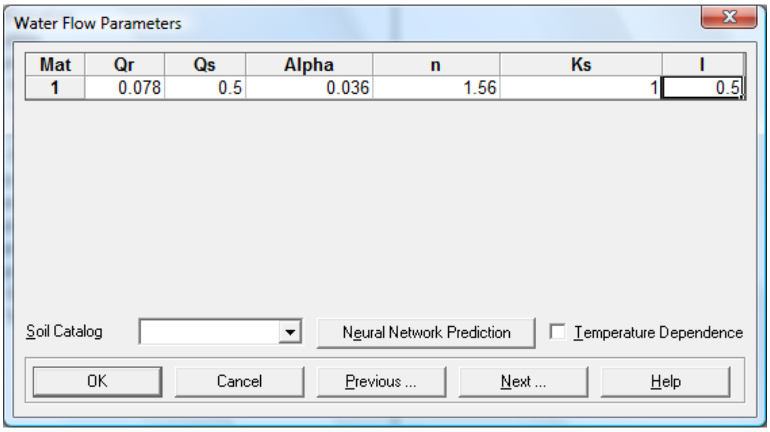
Soil Hydraulic Models

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:



Mat	Qr	Qs	Alpha	n	Ks	l
1	0.078	0.5	0.036	1.56	1	0.5

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

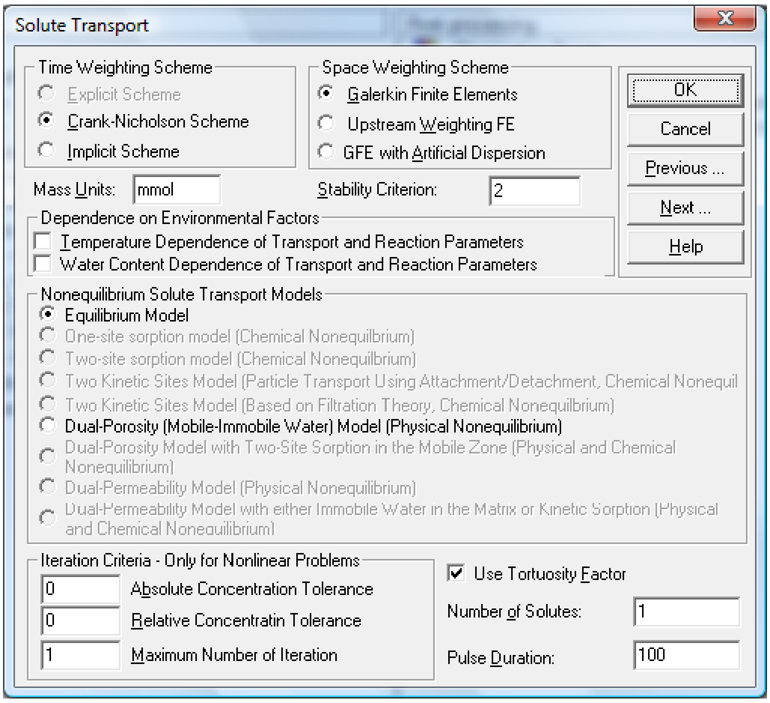
Steady-state flow with infiltration rate of 1 cm/d is given with h=0 at the upper and lower boundaries and with Ks = 1 cm/d. Since θs = 0.5, the pore water velocity *v* is 2 cm/d.

Water Flow Boundary Condition

Upper Boundary Condition: Constant Pressure Head

Lower Boundary Condition: Constant Pressure Head

Solute Transport – General Information



Time Weighting Scheme
- ○ Explicit Scheme
- ● Crank-Nicholson Scheme
- ○ Implicit Scheme

Space Weighting Scheme
- ● Galerkin Finite Elements
- ○ Upstream Weighting FE
- ○ GFE with Artificial Dispersion

Mass Units: mmol

Stability Criterion: 2

Dependence on Environmental Factors
- ☐ Temperature Dependence of Transport and Reaction Parameters
- ☐ Water Content Dependence of Transport and Reaction Parameters

Nonequilibrium Solute Transport Models
- ● Equilibrium Model
- ○ One-site sorption model (Chemical Nonequilibrium)
- ○ Two-site sorption model (Chemical Nonequilibrium)
- ○ Two Kinetic Sites Model (Particle Transport Using Attachment/Detachment, Chemical Nonequil
- ○ Two Kinetic Sites Model (Based on Filtration Theory, Chemical Nonequilibrium)
- ○ 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
- 0 Absolute Concentration Tolerance
- 0 Relative Concentratin Tolerance
- 1 Maximum Number of Iteration

☑ Use Tortuosity Factor

Number of Solutes: 1

Pulse Duration: 100

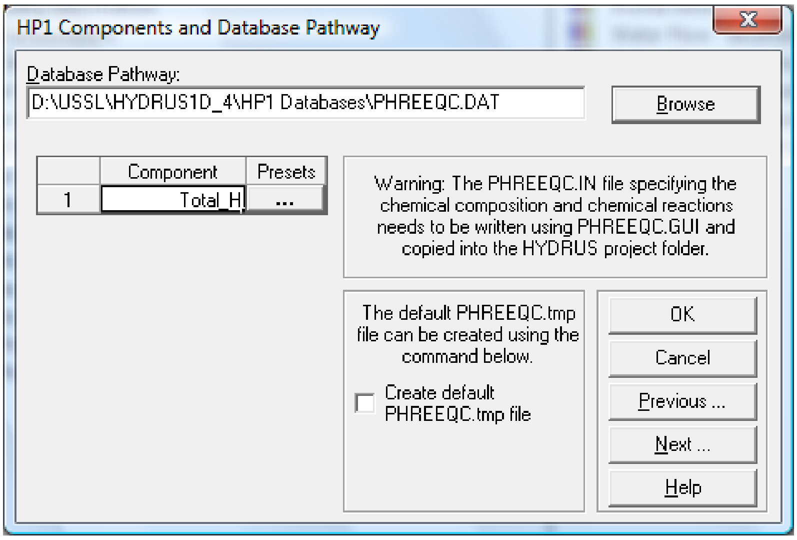
Note: When using HP 1 code, we only have to specify the "Mass Units", the "Number of Solutes" and the "Pulse Duration" options! Leave other values on default.

Mass Units: **mmol**

Number of Solutes: **1**

Pulse Duration: **100**

HP1 Components and Database Pathway



Database Pathway: D:\USSL\HYDRUS1D_4\HP1 Databases\PHREEQC.DAT

	Component	Presets
1	Total_H	...

Warning: The PHREEQC.IN file specifying the chemical composition and chemical reactions needs to be written using PHREEQC.GUI and copied into the HYDRUS project folder.

The default PHREEQC.tmp file can be created using the command below.

☐ Create default PHREEQC.tmp file

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/cm^3**

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.

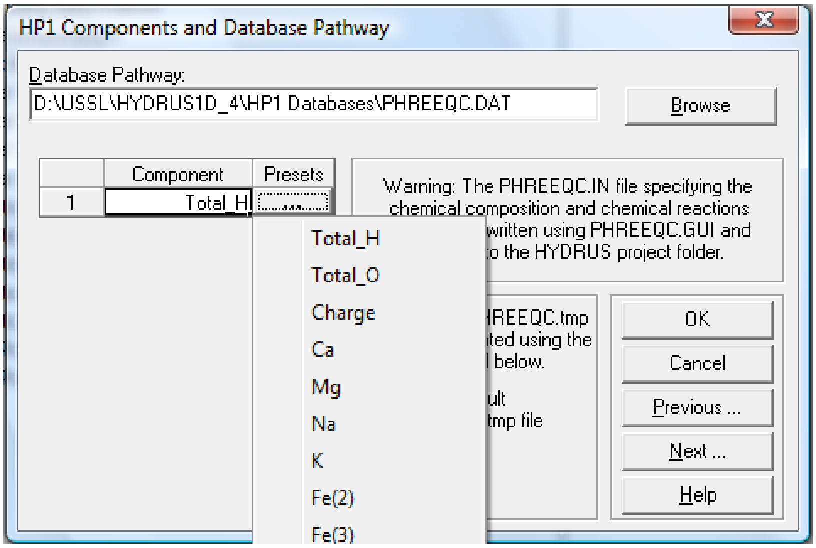
Menu: File->Save Data

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



HP1 Components and Database Pathway

Database Pathway: D:\USSL\HYDRUS1D_4\HP1 Databases\PHREEQC.DAT

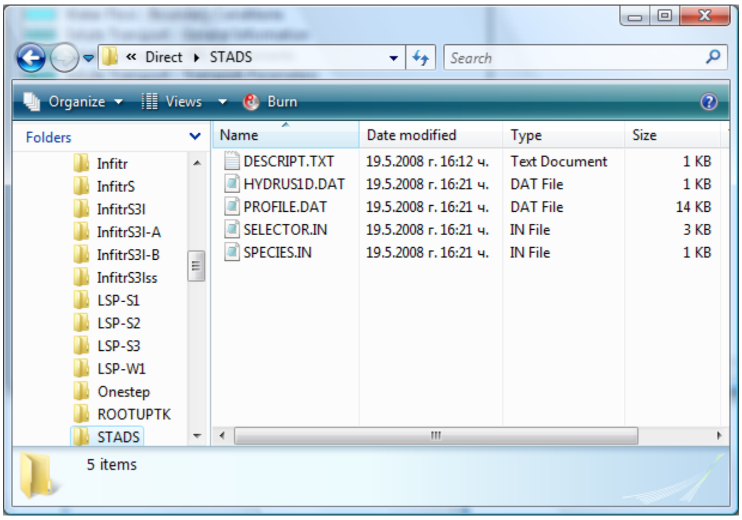
	Component	Presets
1	Total_H	...

Warning: The PHREEQC.IN file specifying the chemical composition and chemical reactions
written using PHREEQC.GUI and
o the HYDRUS project folder.

HREEQC.tmp
ted using the
below.
ult
tmp 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

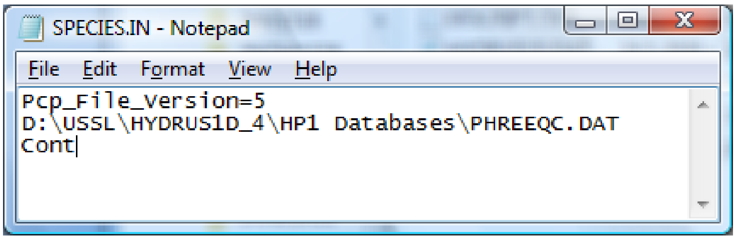


« Direct ▸ STADS

Name	Date modified	Type	Size
DESCRIPT.TXT	19.5.2008 г. 16:12 ч.	Text Document	1 KB
HYDRUS1D.DAT	19.5.2008 г. 16:21 ч.	DAT File	1 KB
PROFILE.DAT	19.5.2008 г. 16:21 ч.	DAT File	14 KB
SELECTOR.IN	19.5.2008 г. 16:21 ч.	IN File	3 KB
SPECIES.IN	19.5.2008 г. 16:21 ч.	IN File	1 KB

5 items

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



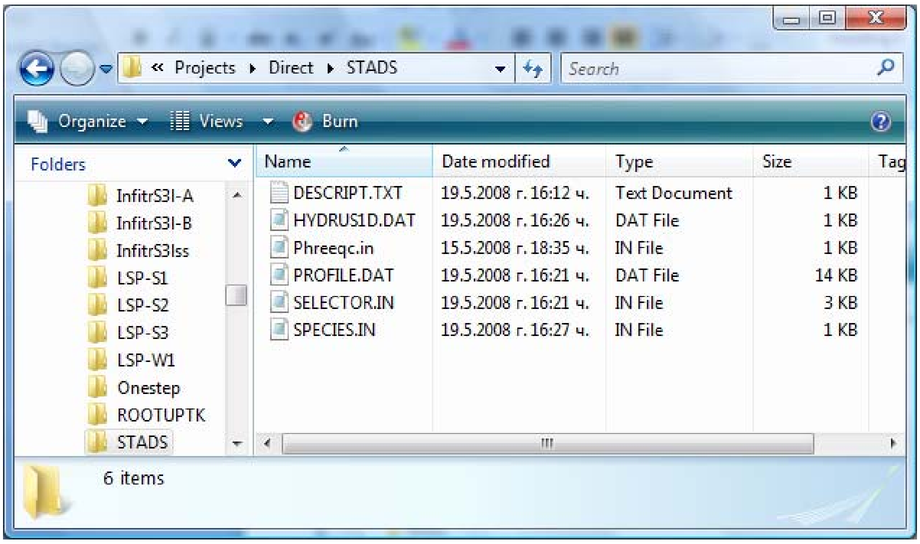
```
Pcp_File_Version=5
D:\USSL\HYDRUS1D_4\HP1 Databases\PHREEQC.DAT
Cont
```

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

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

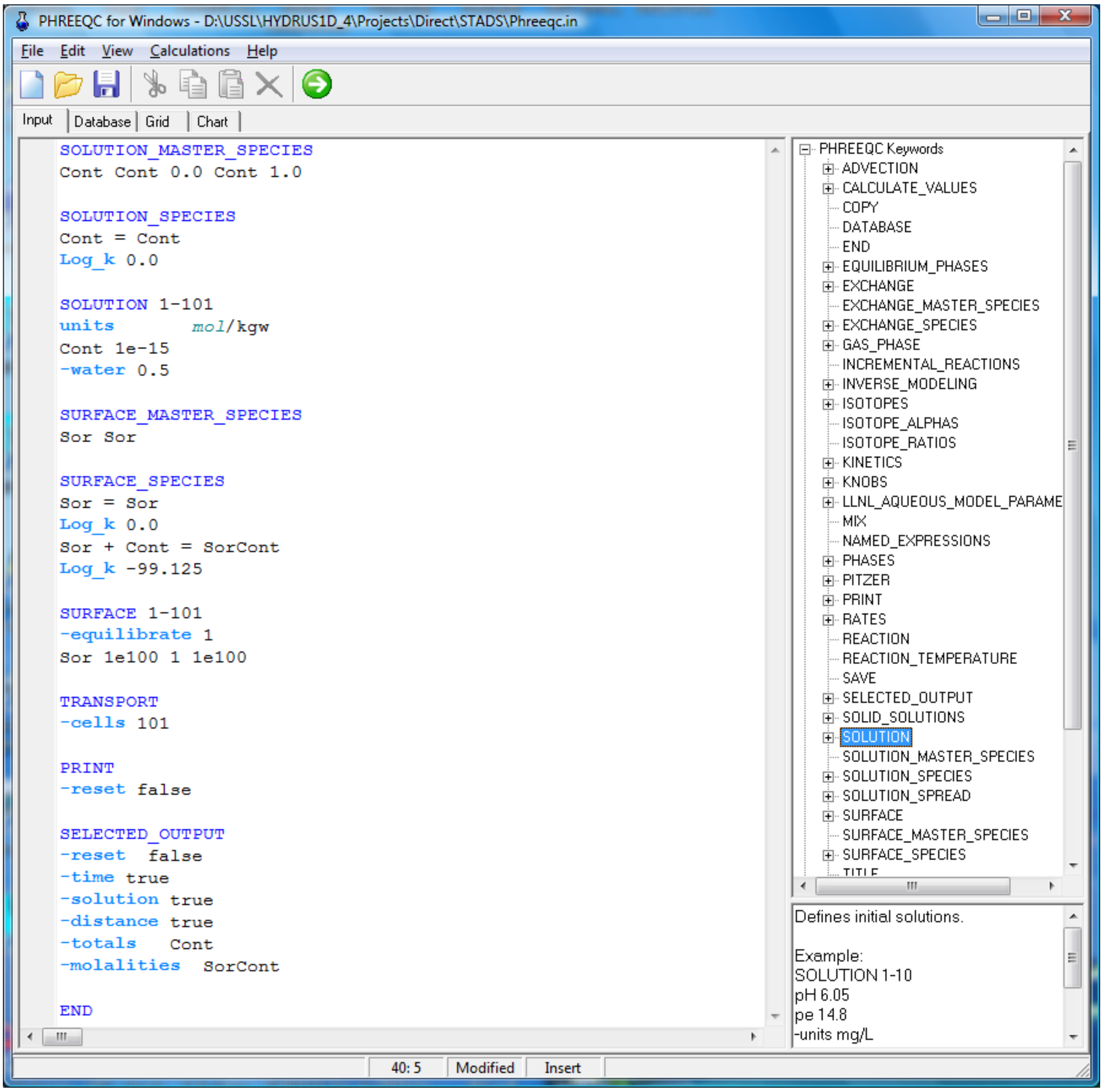
II. PHREEQC module settings

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".



Name	Date modified	Type	Size	Tag
DESCRIPT.TXT	19.5.2008 г. 16:12 ч.	Text Document	1 KB	
HYDRUS1D.DAT	19.5.2008 г. 16:26 ч.	DAT File	1 KB	
Phreeqc.in	15.5.2008 г. 18:35 ч.	IN File	1 KB	
PROFILE.DAT	19.5.2008 г. 16:21 ч.	DAT File	14 KB	
SELECTOR.IN	19.5.2008 г. 16:21 ч.	IN File	3 KB	
SPECIES.IN	19.5.2008 г. 16:27 ч.	IN File	1 KB	

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



```
SOLUTION_MASTER_SPECIES
Cont Cont 0.0 Cont 1.0

SOLUTION_SPECIES
Cont = Cont
Log_k 0.0

SOLUTION 1-101
units          mol/kgw
Cont 1e-15
-water 0.5

SURFACE_MASTER_SPECIES
Sor Sor

SURFACE_SPECIES
Sor = Sor
Log_k 0.0
Sor + Cont = SorCont
Log_k -99.125

SURFACE 1-101
-equilibrate 1
Sor 1e100 1 1e100

TRANSPORT
-cells 101

PRINT
-reset false

SELECTED_OUTPUT
-reset   false
-time true
-solution true
-distance true
-totals    Cont
-molalities   SorCont

END
```

Defines initial solutions.

Example:
SOLUTION 1-10
pH 6.05
pe 14.8
-units mg/L

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 names and aqueous master species.
Cont Cont 0.0 Cont 1.0	Element name (*this is the name from the listbox*), master species (*formula for the master species, including its charge*), 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 (*log_k)* for each aqueous species.
Cont = Cont	Association reaction for aqueous species. The defined species 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****).*
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).
Cont 1e-15	Element list (*an element name, which must correspond to the items in the first column in SOLUTION_MASTER_SPECIES*), initial concentration (***note that*** *it is recommended to enter some very small concentration instead of zero, otherwise the PHREEQC could ignore Cont*).
-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 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.
Sor = Sor	Association reaction for surface species. The defined species 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).*
Sor + Cont = SorCont	Association reaction for the mass action Equation (6) (***note that*** *as we use surface complexation reaction, here is the place for the reaction*).
log_k -99.125	*log_k (***note that** $k = K_d^w$*).*
SURFACE 1-101	This keyword is used to define the amount and composition of each surface in a surface assemblage
-equilibrate 1	Number (*"-equilibrate" indicates that the surface 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*).
Sor 1e100 1 1e100	Surface binding-site name (*name of the surface binding site*), sites (*total number of sites for this binding site, in moles*), 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"*).
TRANSPORT	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 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.
-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.
-reset false	Changes all print options (identifiers) listed on lines 2 through 15 to **true** or **false** (see 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.

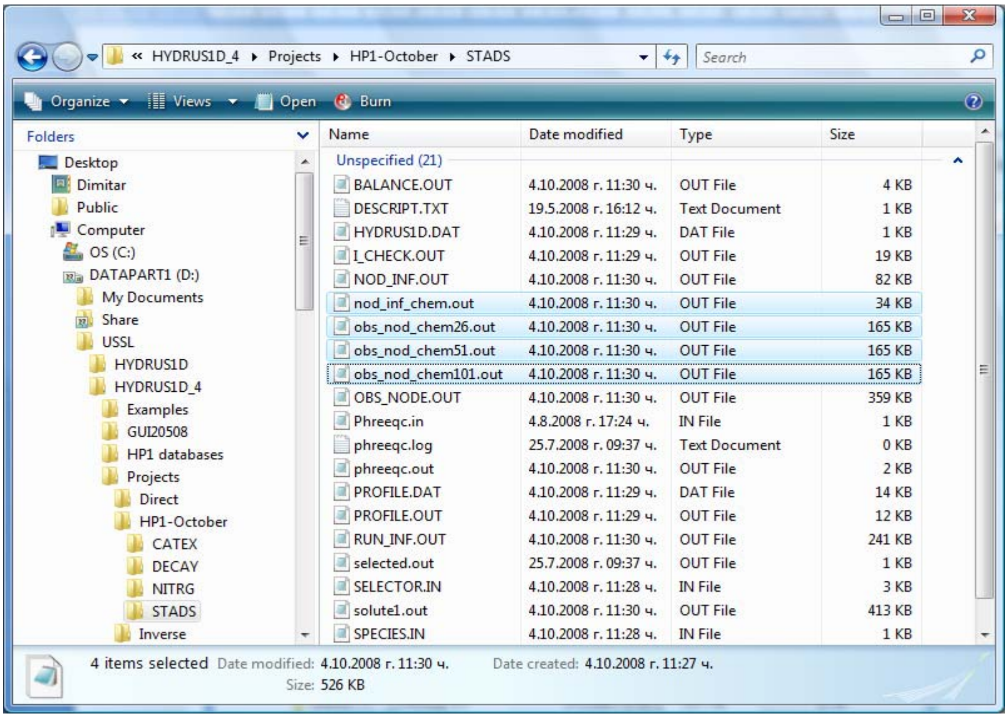
SELECTED_OUTPUT	This keyword data block is used to produce a file that is suitable for processing by spreadsheets and other data-management software.
-reset false	Change print options for all identifiers from line 6 to line 20 (*if the statement "false" is used only the identifiers marked "true" will be printed (see PHREEQC Manual, p. 137*)
-time true	Prints to the selected–output file the cumulative transport time 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.
-distance true	Prints to the selected-output file the X-coordinate of the cell.
-totals Cont	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 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 *Cont* in the solution phase.
-molalities SorCont	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*). Species must have been defined by SOLUTION_SPECIES, EXCHANGE_SPECIES, or SURFACE_SPECIES input. In the example, we define the adsorbed concentration of *Cont* 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.

When the program finishes, open the STADS folder:



Name	Date modified	Type	Size
Unspecified (21)			
BALANCE.OUT	4.10.2008 г. 11:30 ч.	OUT File	4 KB
DESCRIPT.TXT	19.5.2008 г. 16:12 ч.	Text Document	1 KB
HYDRUS1D.DAT	4.10.2008 г. 11:29 ч.	DAT File	1 KB
I_CHECK.OUT	4.10.2008 г. 11:29 ч.	OUT File	19 KB
NOD_INF.OUT	4.10.2008 г. 11:30 ч.	OUT File	82 KB
nod_inf_chem.out	4.10.2008 г. 11:30 ч.	OUT File	34 KB
obs_nod_chem26.out	4.10.2008 г. 11:30 ч.	OUT File	165 KB
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
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
selected.out	25.7.2008 г. 09:37 ч.	OUT File	1 KB
SELECTOR.IN	4.10.2008 г. 11:28 ч.	IN File	3 KB
solute1.out	4.10.2008 г. 11:30 ч.	OUT File	413 KB
SPECIES.IN	4.10.2008 г. 11:28 ч.	IN File	1 KB

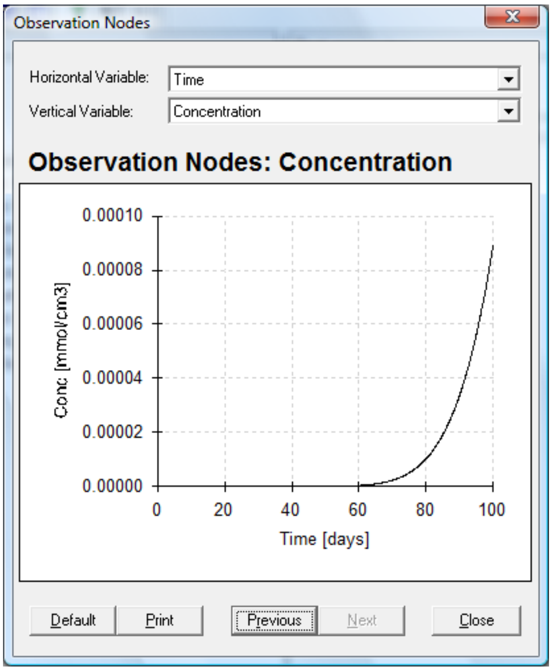
4 items selected Date modified: 4.10.2008 г. 11:30 ч. Date created: 4.10.2008 г. 11:27 ч.
Size: 526 KB

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:

<u>Post-processing</u>

Observation Points

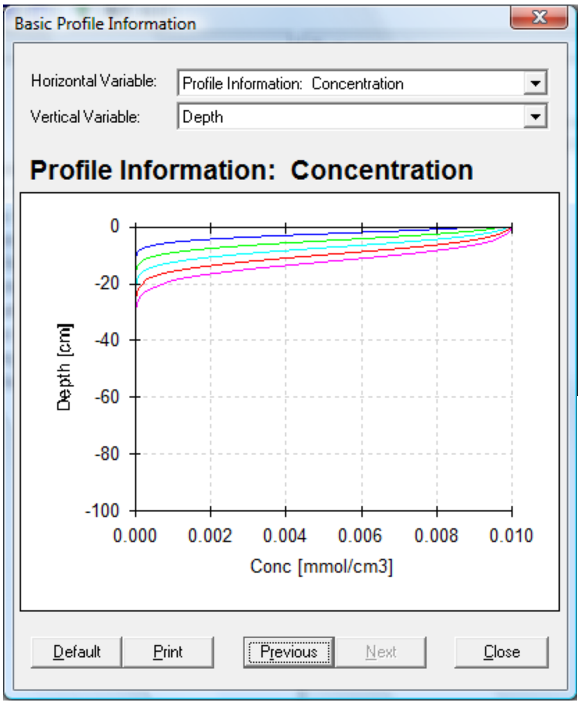


Horizontal Variable: Time

Vertical Variable: Concentration

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



These graphs show the *Cont* concentration distribution through the profile at the initial plus at the printed time steps (four in the example). At the last time step (100 d, the light red graph) the concentration through the whole profile is equal to the zerot at the 30 cm.

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 [L^3M^{-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:

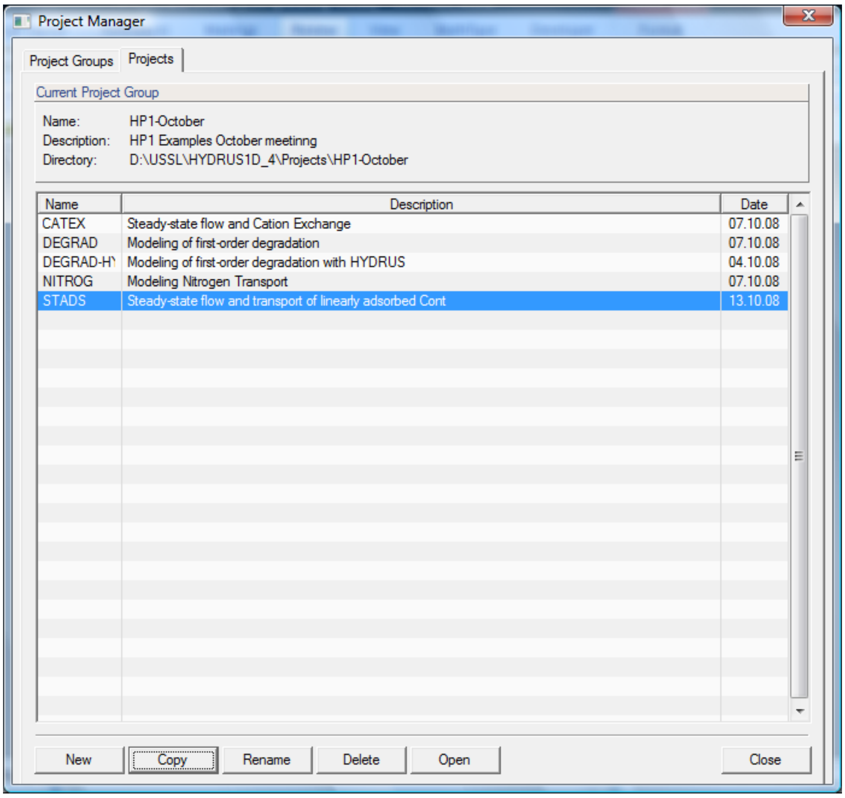
$$K_d^w = \frac{[SorCont]}{[Sor][Cont]^{n_F}} \qquad (11)$$

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

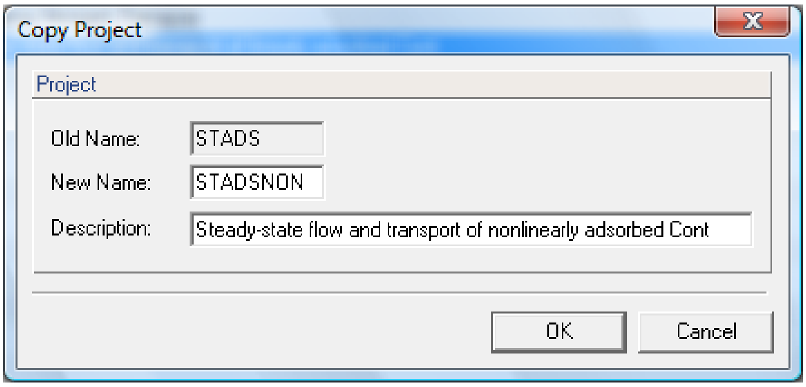


Name: HP1-October
Description: HP1 Examples October meetinng
Directory: D:\USSL\HYDRUS1D_4\Projects\HP1-October

Name	Description	Date
CATEX	Steady-state flow and Cation Exchange	07.10.08
DEGRAD	Modeling of first-order degradation	07.10.08
DEGRAD-H	Modeling of first-order degradation with HYDRUS	04.10.08
NITROG	Modeling Nitrogen Transport	07.10.08
STADS	Steady-state flow and transport of linearly adsorbed Cont	13.10.08

Click on "STADS" project

Button: "Copy"



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

New Name: STADSNON

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

Button: "OK"

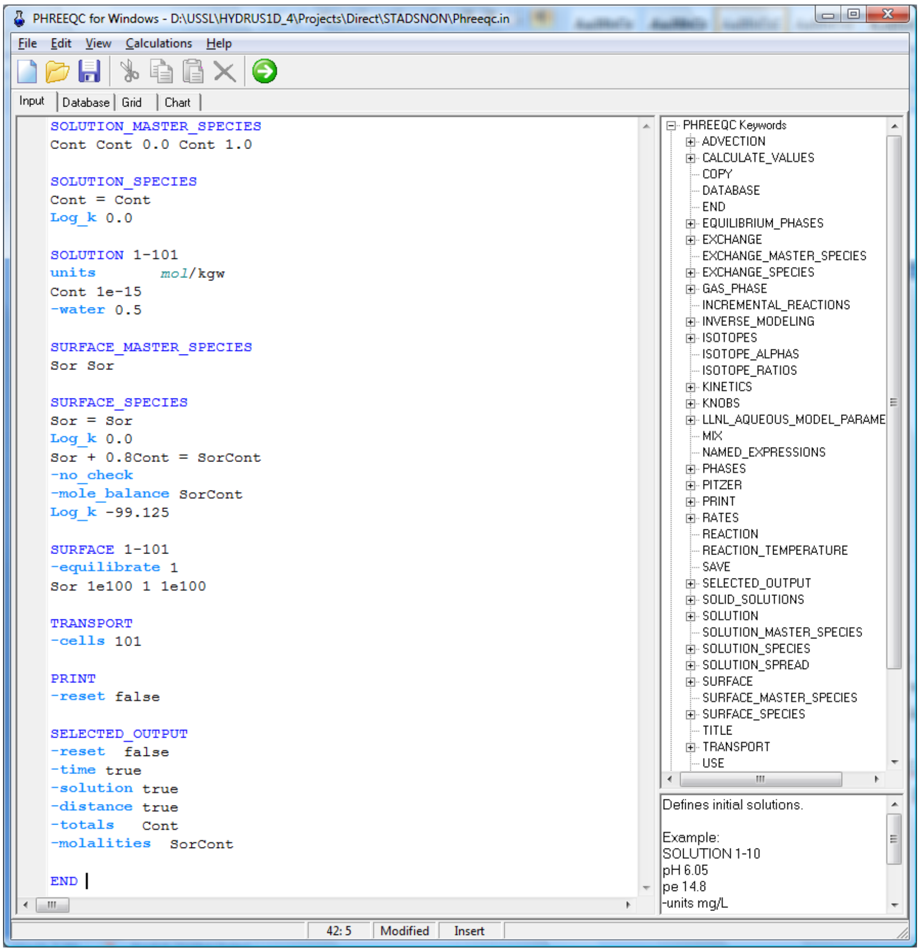
Button: "Open" from "Project Manager" window

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:



```
SOLUTION_MASTER_SPECIES
Cont Cont 0.0 Cont 1.0

SOLUTION_SPECIES
Cont = Cont
Log_k 0.0

SOLUTION 1-101
units         mol/kgw
Cont 1e-15
-water 0.5

SURFACE_MASTER_SPECIES
Sor Sor

SURFACE_SPECIES
Sor = Sor
Log_k 0.0
Sor + 0.8Cont = SorCont
-no_check
-mole_balance SorCont
Log_k -99.125

SURFACE 1-101
-equilibrate 1
Sor 1e100 1 1e100

TRANSPORT
-cells 101

PRINT
-reset false

SELECTED_OUTPUT
-reset  false
-time true
-solution true
-distance true
-totals   Cont
-molalities  SorCont

END
```

Defines initial solutions.

Example:
SOLUTION 1-10
pH 6.05
pe 14.8
-units mg/L

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

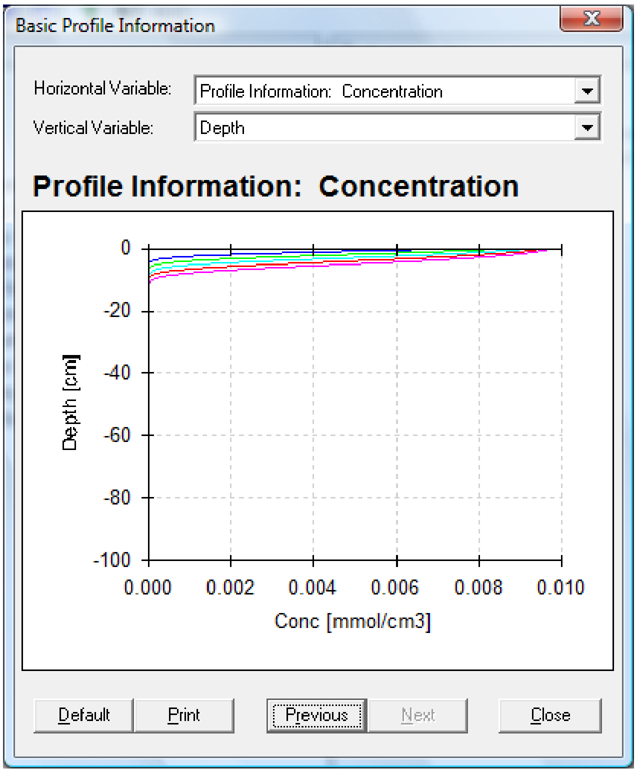
Save "Phreeqc.in" file and execute HP 1:

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 $CaCl_2$ (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 $CaCl_2$ is 0.006 mol/kgw (0.006 mmol/cm^3). 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:

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

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}], θθ is the volumetric water content [L^{3}L^{-3}], q is the water flux [LT^{-1}] and D^w is the diffusion-dispersion coefficient (L^{2}T^{-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:

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

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

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

$$\frac{\partial C_{l,K}}{\partial t} = \frac{\partial}{\partial x}\left(D^w_{K} \frac{\partial C_{l,K}}{\partial x} \right) - \frac{q}{\theta}\frac{\partial C_{l,K}}{\partial x} + R_{K} \qquad (5)$$

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:

$0.5Ca^{2+} + Na\text{-}X \leftrightarrow 0.5Ca\text{-}X_2 + Na^+$ (6)

with equilibrium constant $K_{Ca/Na} = \dfrac{\left[\mathrm{CaX_2}\right]^{0.5}\left[\mathrm{Na^+}\right]}{\left[\mathrm{NaX}\right]\left[\mathrm{Ca^{2+}}\right]^{0.5}}$ (7)

$0.5Ca^{2+} + K\text{-}X \leftrightarrow 0.5Ca\text{-}X_2 + K^+$ (8)

with equilibrium constant $K_{Ca/K} = \dfrac{\left[\mathrm{CaX_2}\right]^{0.5}\left[\mathrm{K^+}\right]}{\left[\mathrm{KX}\right]\left[\mathrm{Ca^{2+}}\right]^{0.5}}$ (9)

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

with equilibrium constant $K_{K/Na} = \dfrac{\left[\mathrm{KX}\right]\left[\mathrm{Na^+}\right]}{\left[\mathrm{NaX}\right]\left[\mathrm{K^+}\right]}$ (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.

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:

$[Ca\text{-}X_2] + [Na\text{-}X] + [K\text{-}X] = CEC$ (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 so-called ***half reaction terms***:

$Ca^{2+} + 2X^- \leftrightarrow Ca\text{-}X_2$ (13)

with equilibrium constant $K_{Ca} = \dfrac{\left[\mathrm{CaX_2}\right]}{\left[\mathrm{Ca^{2+}}\right]\left[\mathrm{X^-}\right]^2} = 6.31$ (14)

$Na^+ + X^- \leftrightarrow Na\text{-}X$ (15)

with equilibrium constant $K_{Na} = \dfrac{\left[\mathrm{NaX}\right]}{\left[\mathrm{Na^+}\right]\left[\mathrm{X^-}\right]} = 1.00$ (16)

$K^+ + X^- \leftrightarrow K\text{-}X$ (17)

with equilibrium constant $K_K = \dfrac{\left[\mathrm{KX}\right]}{\left[\mathrm{K^+}\right]\left[\mathrm{X^-}\right]} = 5.01$ (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:

$$\frac{\left[\mathrm{CaX_2}\right]^{0.5}\left[\mathrm{Na^+}\right]}{\left[\mathrm{NaX}\right]\left[\mathrm{Ca^{2+}}\right]^{0.5}} = \frac{K_{Ca}^{0.5}}{K_{Na}} = 2.5119 \quad (19)$$

where the term $K_{Ca}^{0.5}/K_{Na}$ represents the equilibrium constant $K_{Ca/Na}$ 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 cm^3, the CEC in the PHREEQC module is express always as concentration [mol/1000 cm^3] 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 cm^3* (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/L^3] = CEC [M/L^3], thus, it could be said that the CEC dimension in HP 1 is *moles per 1000 cm^3 soil*.
So, in the example CEC =0.73 [$mmol_c$/kg soil] and ρ_b = 1.5[g/cm^3], therefore CEC in M/L^3 = 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).

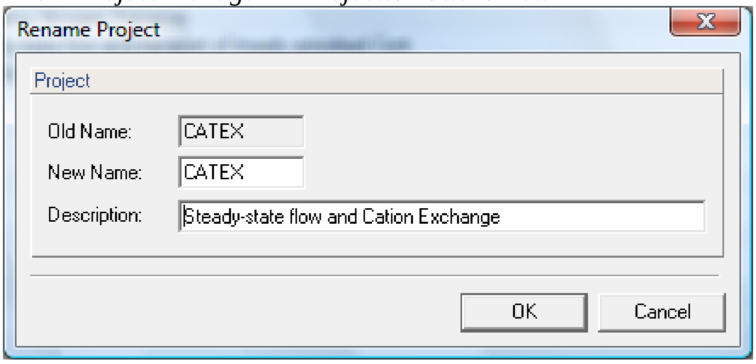
Note that the initial composition is in equilibrium with the exchange sites in the beginning of the simulation. The values of initial solution are: Na 1.0E-04, K 2.0 E-05, Ca 1.0E-10 (note that there is a need of nonzero value) and Cl 1.2E-04 all in *mol per kilogram water (or litre).* The values of 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**.

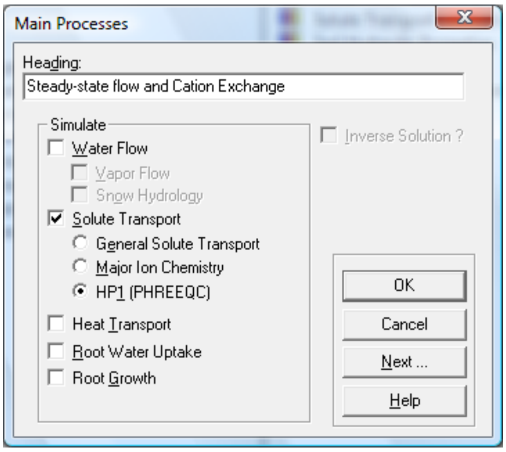
HYDRUS-1D module settings

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



Old Name: CATEX
New Name: CATEX
Description: Steady-state flow and Cation Exchange

Main Processes



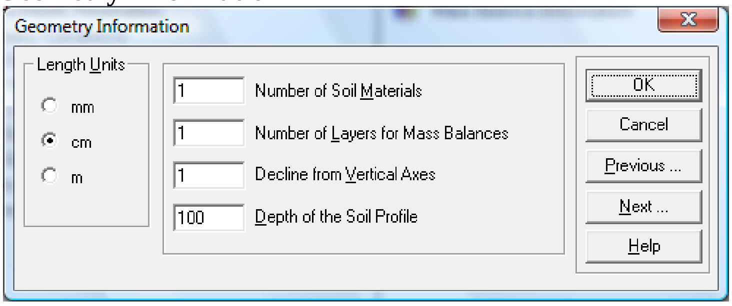
Heading:
Steady-state flow and Cation Exchange

Simulate
☐ Water Flow
  ☐ Vapor Flow
  ☐ Snow Hydrology
☑ Solute Transport
  ○ General Solute Transport
  ○ Major Ion Chemistry
  ● HP1 (PHREEQC)
☐ Heat Transport
☐ Root Water Uptake
☐ Root Growth

☐ Inverse Solution ?

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

Geometry Information

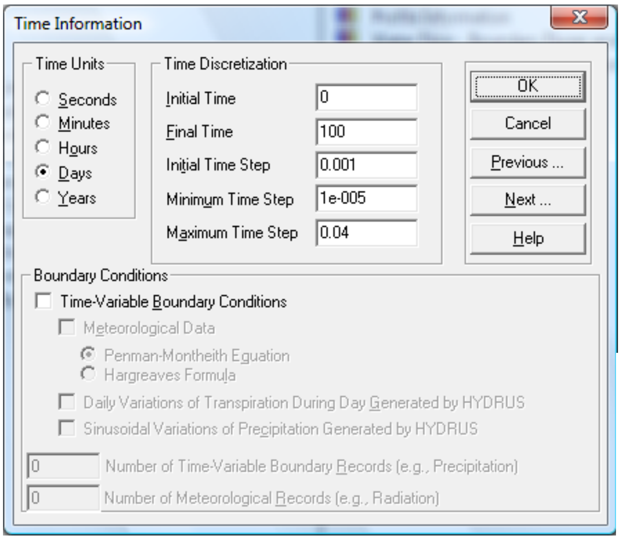


Length Units
○ mm
● cm
○ m

1 Number of Soil Materials
1 Number of Layers for Mass Balances
1 Decline from Vertical Axes
100 Depth of the Soil Profile

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

Time Information



Time Units
- ○ Seconds
- ○ Minutes
- ○ Hours
- ● Days
- ○ Years

Time Discretization
- Initial Time: 0
- Final Time: 100
- Initial Time Step: 0.001
- Minimum Time Step: 1e-005
- Maximum Time Step: 0.04

Boundary Conditions
- ☐ Time-Variable Boundary Conditions
  - ☐ Meteorological Data
    - ● Penman-Montheith Equation
    - ○ Hargreaves Formula
  - ☐ Daily Variations of Transpiration During Day Generated by HYDRUS
  - ☐ Sinusoidal Variations of Precipitation Generated by HYDRUS
- 0 Number of Time-Variable Boundary Records (e.g., Precipitation)
- 0 Number of Meteorological Records (e.g., Radiation)

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

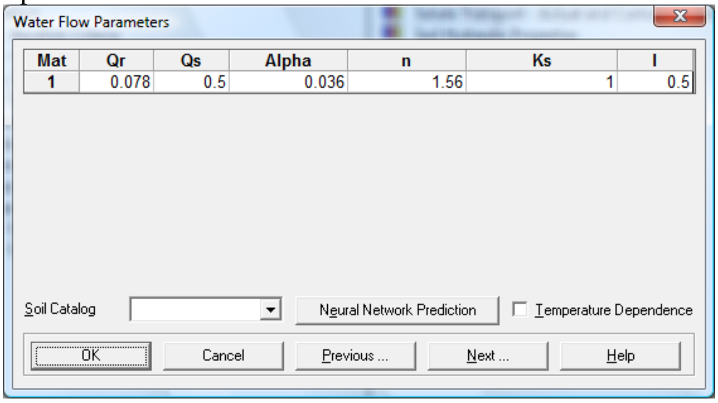
Note: Leave all options on default

Soil Hydraulic Models

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

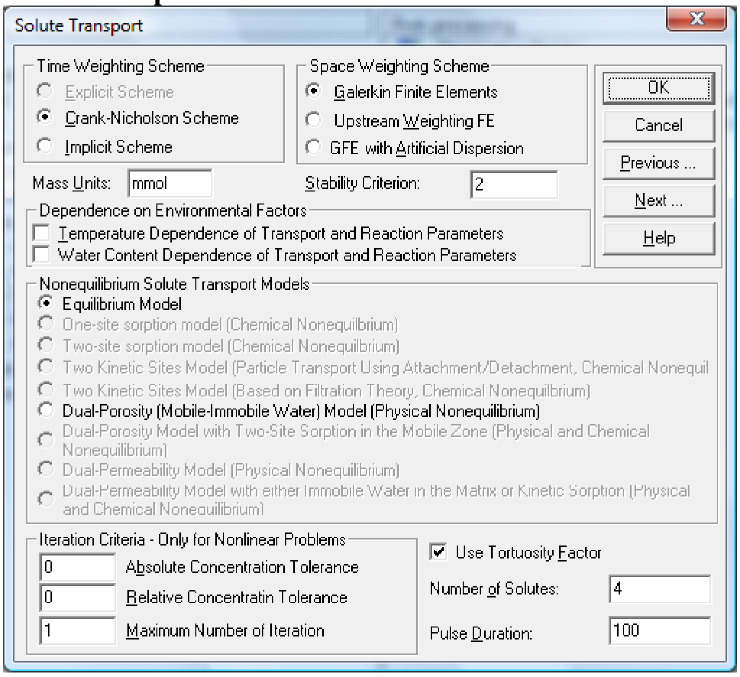
Water Flow Parameters

Input the data as shown below:



Mat	Qr	Qs	Alpha	n	Ks	l
1	0.078	0.5	0.036	1.56	1	0.5

Solute Transport – General Information



Time Weighting Scheme
○ Explicit Scheme
● Crank-Nicholson Scheme
○ Implicit Scheme

Space Weighting Scheme
● Galerkin Finite Elements
○ Upstream Weighting FE
○ GFE with Artificial Dispersion

Mass Units: mmol
Stability Criterion: 2

Dependence on Environmental Factors
☐ Temperature Dependence of Transport and Reaction Parameters
☐ Water Content Dependence of Transport and Reaction Parameters

Nonequilibrium Solute Transport Models
● Equilibrium Model
○ One-site sorption model (Chemical Nonequilibrium)
○ Two-site sorption model (Chemical Nonequilbrium)
○ Two Kinetic Sites Model (Particle Transport Using Attachment/Detachment, Chemical Nonequil
○ Two Kinetic Sites Model (Based on Filtration Theory, Chemical Nonequilbrium)
○ 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)

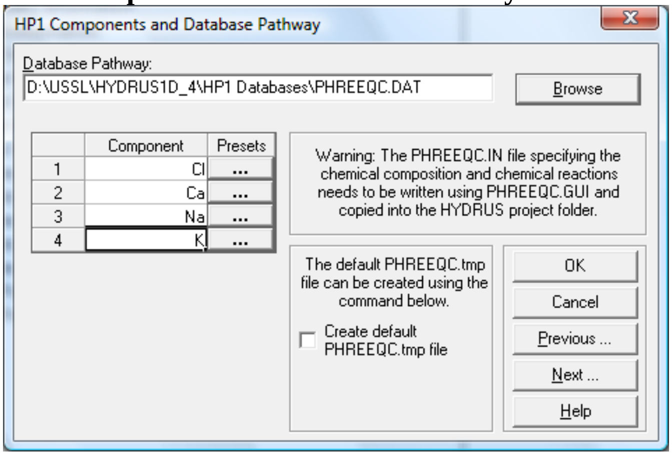
Iteration Criteria - Only for Nonlinear Problems
0 Absolute Concentration Tolerance
0 Relative Concentratin Tolerance
1 Maximum Number of Iteration

☑ Use Tortuosity Factor
Number of Solutes: 4
Pulse Duration: 100

Mass Units: **mmol**
Number of Solutes: **4**
Pulse Duration: **100 days**

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

HP1 Components and Database Pathway



Database Pathway: D:\USSL\HYDRUS1D_4\HP1 Databases\PHREEQC.DAT

	Component	Presets
1	Cl	...
2	Ca	...
3	Na	...
4	K	...

Warning: The PHREEQC.IN file specifying the chemical composition and chemical reactions needs to be written using PHREEQC.GUI and copied into the HYDRUS project folder.

The default PHREEQC.tmp file can be created using the command below.

☐ Create default PHREEQC.tmp file

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.

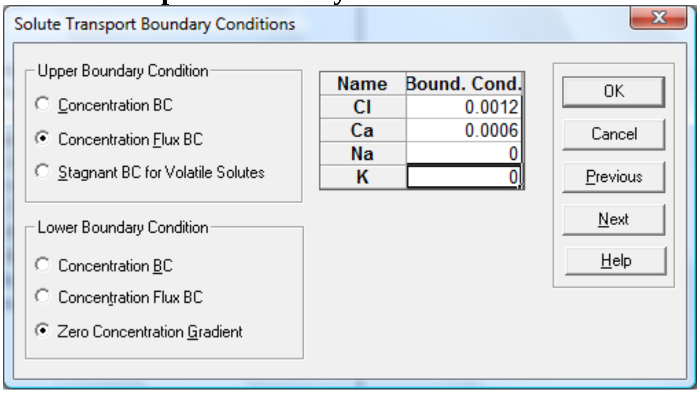
Solute Transport - Transport Parameters

Bulk D.: **1.5 g/cm^3**
Disp.: **1 cm**
Difus. W. /diffusion coefficient in free water/**: 0 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



Solute Transport Boundary Conditions

Upper Boundary Condition
○ Concentration BC
● Concentration Flux BC
○ Stagnant BC for Volatile Solutes

Lower Boundary Condition
○ Concentration BC
○ Concentration Flux BC
● Zero Concentration Gradient

Name	Bound. Cond.
Cl	0.0012
Ca	0.0006
Na	0
K	0

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.

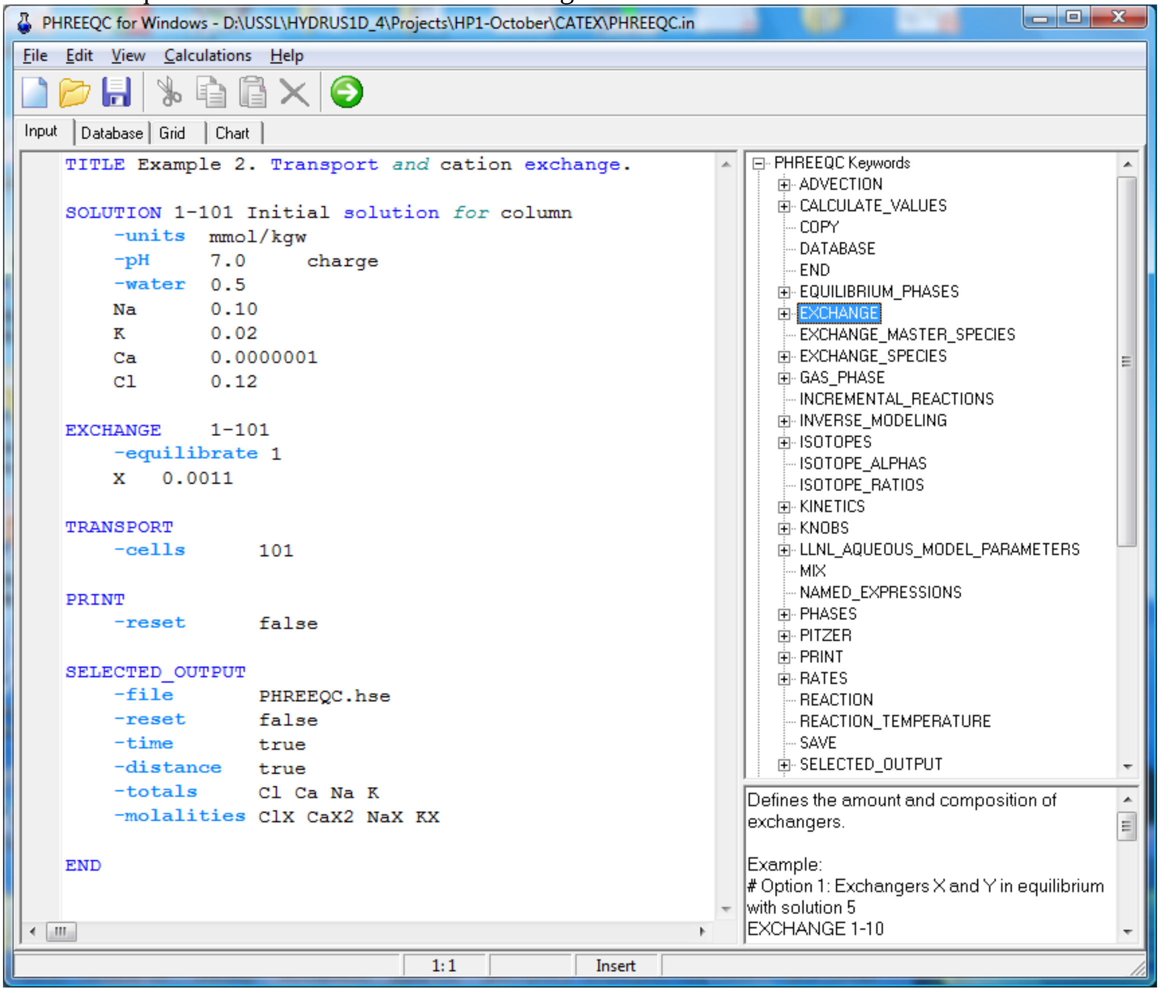
Note that even though we have Initial conditions of the concentrations (the Na-K-Cl solution), we must define them in the PHREEQC module and not here!

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:



```
TITLE Example 2. Transport and cation exchange.

SOLUTION 1-101 Initial solution for column
    -units   mmol/kgw
    -pH      7.0      charge
    -water   0.5
    Na       0.10
    K        0.02
    Ca       0.0000001
    Cl       0.12

EXCHANGE     1-101
    -equilibrate 1
    X    0.0011

TRANSPORT
    -cells       101

PRINT
    -reset       false

SELECTED_OUTPUT
    -file        PHREEQC.hse
    -reset       false
    -time        true
    -distance    true
    -totals      Cl  Ca  Na  K
    -molalities  ClX  CaX2  NaX  KX

END
```

Defines the amount and composition of exchangers.

Example:
Option 1: Exchangers X and Y in equilibrium with solution 5
EXCHANGE 1-10

In this example:

Item	Description (Meaning)
TITLE Example 2. Transport and cation exchange	This keyword data block is used to include a comment for a simulation in 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. (*in fact, we must specify the solution/s for all cells of the modeled profile, in our case 100*). 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 (*millimoles per kilogram water*).
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 (***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.*
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 $\mathbf{X}^-$.
X 0.0011	Exchange site (*only the name of the exchange site needs to be entered*), amount (*quantity of exchange site, in moles*). Note that the dimension is by default always in **moles**. This means that every cell possesses 0.0011 mol of the exchanger (*see the Remark*[1]).
-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).
TRANSPORT	This key data block is used to simulate 1D transport processes. However, 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.
-reset false	Changes all print options listed on lines 2 through 15 to **true** or **false** (*see 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.
SELECTED_OUTPUT	This keyword data block is used to produce a file that is suitable for processing by spreadsheets and other data-management software. The selected-output file contains a column for each data item defined through the identifiers of SELECTED_OUTPUT.
-file PHREEQC.hse	"-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 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.
-reset false	Change print options for all identifiers from line 6 to line 20 (if 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 since the beginning of the run or other defined options.
-distance true	Prints to the selected-output file the X-coordinate of the cell.
-totals Cl Ca Na K	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 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^{2+}, Na^+, and K^+ in the solution phase. Note that the four components exist in the PHREEQC data base.
-molalities ClX CaX2 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*). 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 PHREEQC data base.
END	This keyword ends the data input for a simulation.

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

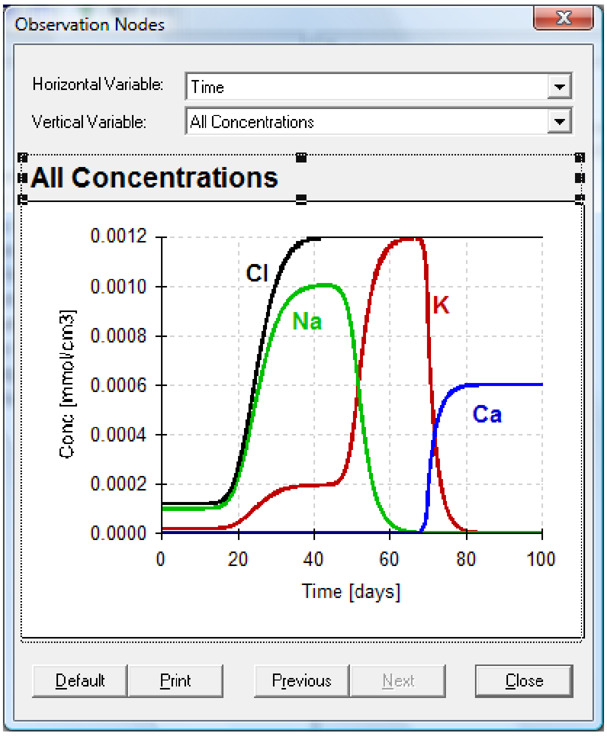
Remark[1]: The number of exchange sites at each node is 0.0011 mol , and the initial composition of the exchanger is calculated such that it is in equilibrium with solution 1, *i.e.* cations Ca^{2+}, Na^{+}, and K^{+} are at all times in equilibrium with the exchanger. In the example, the initial exchange 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

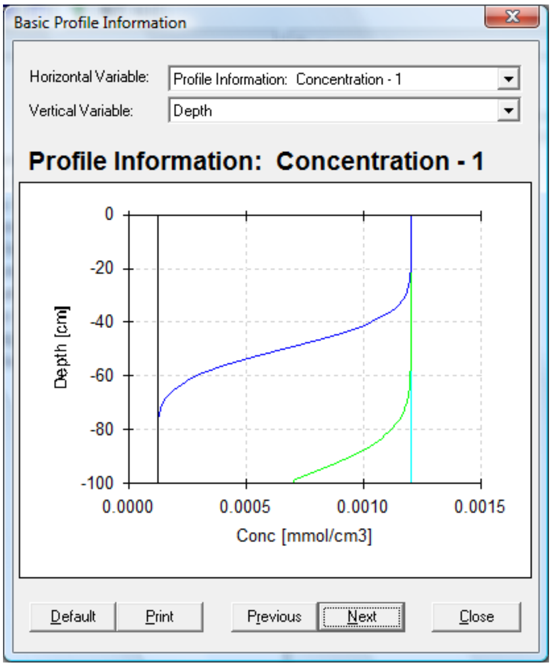
Observation Points



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.

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 **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 **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 **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/cm^{3}) 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 Ca^{2+} cations) and the concentration of calcium increases to a steady-state value equal to the concentration of the applied solution.

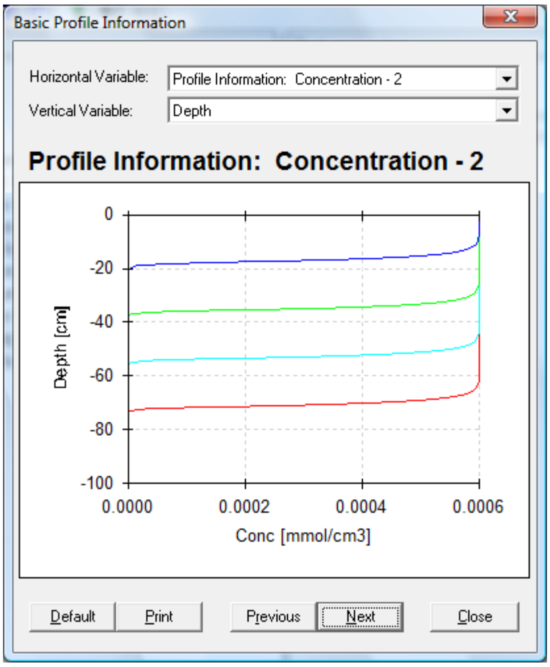
Profile Information



Horizontal Variable: Profile Information: Concentration - 1

Vertical Variable: Depth

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

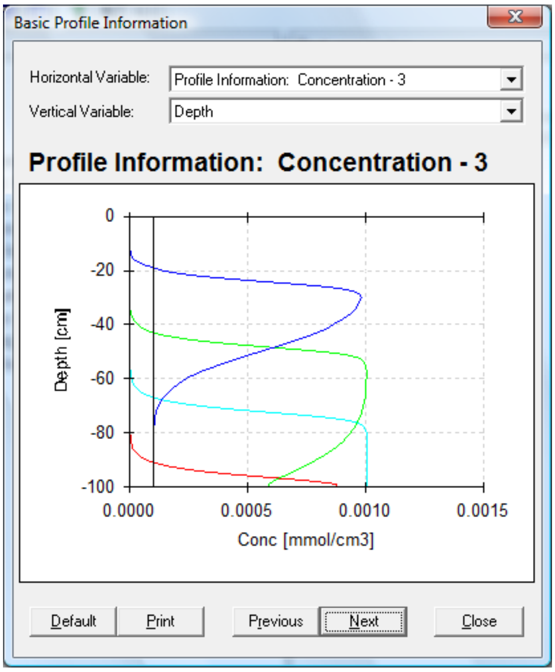


Horizontal Variable: Profile Information: Concentration - 2

Vertical Variable: Depth

The Ca^{2+} concentration in the solute phase through the profile at the initial time (zero value) and at the printed time steps.

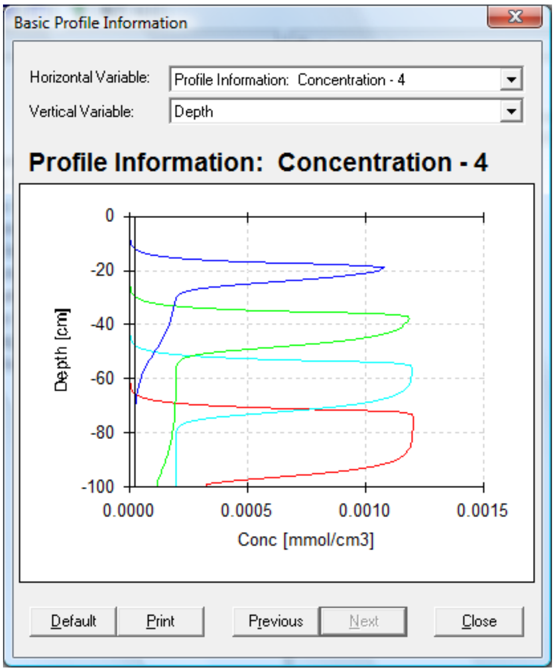
Profile Information



Horizontal Variable: Profile Information: Concentration - 3

Vertical Variable: Depth

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



Horizontal Variable: Profile Information: Concentration - 4

Vertical Variable: Depth

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.

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/cm^3 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/l (0.01 mmol/cm^3). 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 [cm^3/g] for *Contc* (Fig. 1).

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

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

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}], θθ is the volumetric water content [L^{3}L^{-3}], *q* is the flux [LT^{-1}] and D^w is the diffusion-dispersion coefficient (L^{2}T^{-1}), R_i is the general source/sink term due to geochemical reactions for the i^{th} species [ML^{-3}T^{-1}].
In this example, the term R_i considers two type of reactions: adsorption and first-order decay (degradation) process (Fig. 1):

$$R_i^{'} = -\rho_b \frac{\partial C_{a,i}}{\partial t} \qquad (2)$$

and

$$R_i^{''} = -\mu C_i \qquad (3)$$

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 [L^3M^{-1}].

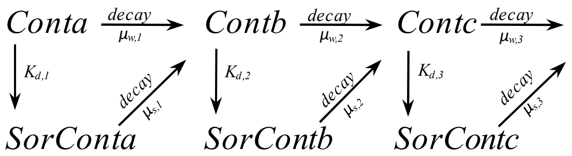


Fig. 1. The processes scheme for first-order decay chain of linearly adsorbed conponents *Conta, Contb and Contc.*

Transport equations for each component are described with:

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

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

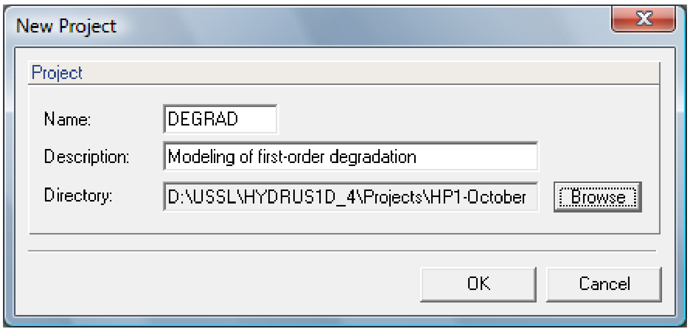
$$\frac{\partial C_{l,Contc}}{\partial t} = \frac{\partial}{\partial x}\left(D^w_{Contc}\frac{\partial C_{l,Contc}}{\partial x}\right) - \frac{q}{\theta}\frac{\partial C_{l,Contc}}{\partial x} - \rho_b K_{d,3}\frac{\partial C_{l,Contc}}{\partial t} + \mu_{w,2}\theta C_{l,Contb} + \mu_{s,2}\rho_b K_{d,2}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

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: ρ_b=1.5 [g/cm^3], $K_{d,1}$ =5.0 [cm^3/g], $K_{d,2}$ =2.5 [cm^3/g], $K_{d,3}$ =0.75 [cm^3/g], [Sor]$_{\mathrm{Total}}$=1E+100 [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***



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

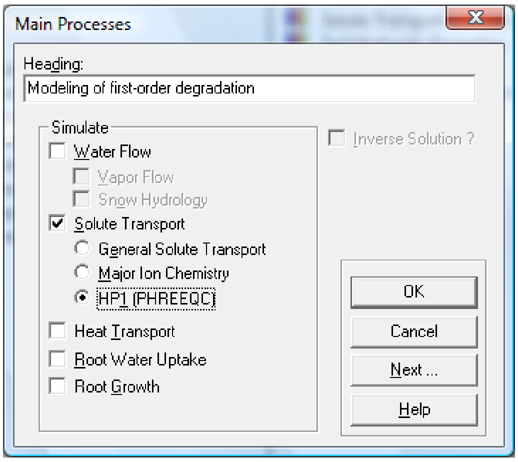
Name: DEGRAD

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



Heading: Modeling of first-order degradation

Simulate
☐ Water Flow
☐ Vapor Flow
☐ Snow Hydrology
☑ Solute Transport
○ General Solute Transport
○ Major Ion Chemistry
● HP1 (PHREEQC)
☐ Heat Transport
☐ Root Water Uptake
☐ Root Growth

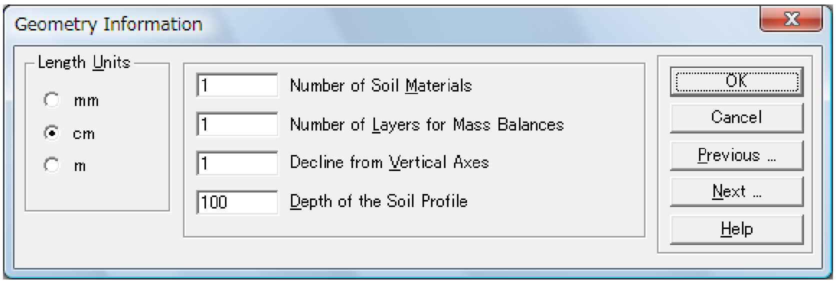
☐ Inverse Solution ?

Heading: Modeling of first-order degradation

Simulate: Solute Transport and check "HP1 (PHREEQC)" option.

Button: "Next"

Geometry Information



Length Units
○ mm
● cm
○ m

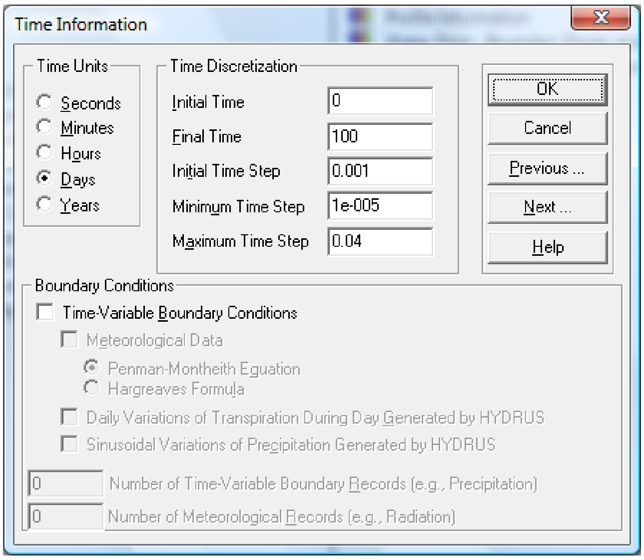
1 Number of Soil Materials
1 Number of Layers for Mass Balances
1 Decline from Vertical Axes
100 Depth of the Soil Profile

Length Units: cm

Depth of the Soil Profile: 100 cm

Button: "Next"

Time Information



Time Units
○ Seconds
○ Minutes
○ Hours
● Days
○ Years

Time Discretization
Initial Time 0
Final Time 100
Initial Time Step 0.001
Minimum Time Step 1e-005
Maximum Time Step 0.04

Boundary Conditions
☐ Time-Variable Boundary Conditions
☐ Meteorological Data
● Penman-Montheith Equation
○ Hargreaves Formula
☐ Daily Variations of Transpiration During Day Generated by HYDRUS
☐ Sinusoidal Variations of Precipitation Generated by HYDRUS
0 Number of Time-Variable Boundary Records (e.g., Precipitation)
0 Number of Meteorological Records (e.g., Radiation)

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

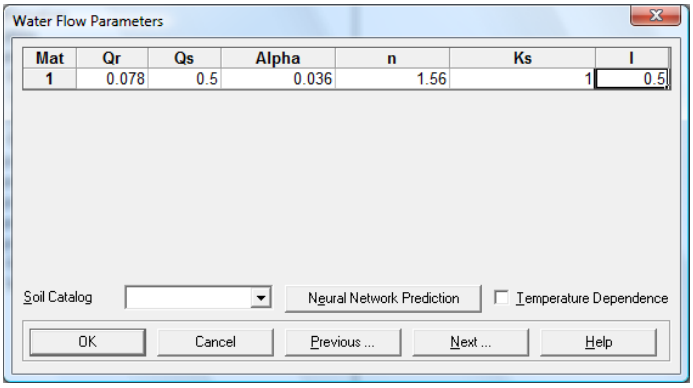
Soil Hydraulic Models

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 Flow Parameters

Mat	Qr	Qs	Alpha	n	Ks	l
1	0.078	0.5	0.036	1.56	1	0.5

Soil Catalog

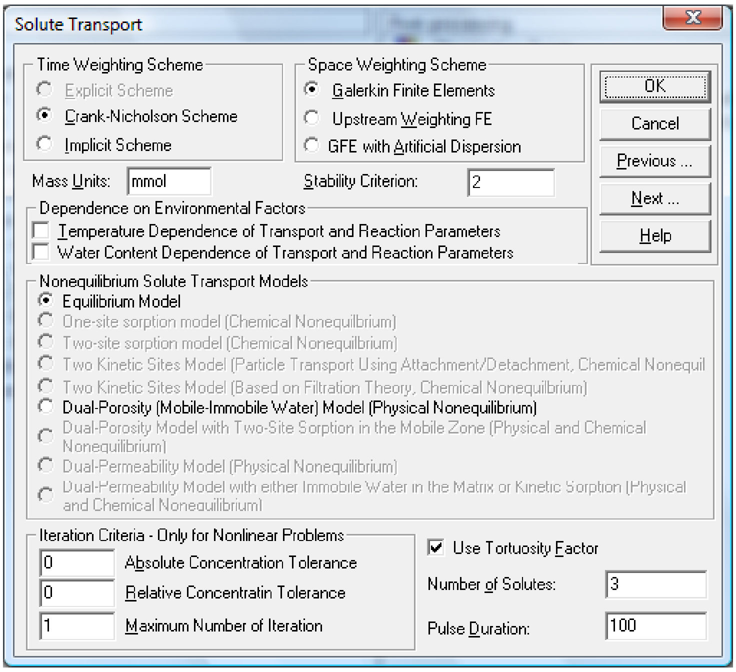
☐ Temperature Dependence

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
- ○ Explicit Scheme
- ● Crank-Nicholson Scheme
- ○ Implicit Scheme

Space Weighting Scheme
- ● Galerkin Finite Elements
- ○ Upstream Weighting FE
- ○ GFE with Artificial Dispersion

Mass Units: mmol

Stability Criterion: 2

Dependence on Environmental Factors
- ☐ Temperature Dependence of Transport and Reaction Parameters
- ☐ Water Content Dependence of Transport and Reaction Parameters

Nonequilibrium Solute Transport Models
- ● Equilibrium Model
- ○ One-site sorption model (Chemical Nonequilbrium)
- ○ Two-site sorption model (Chemical Nonequilbrium)
- ○ Two Kinetic Sites Model (Particle Transport Using Attachment/Detachment, Chemical Nonequil
- ○ Two Kinetic Sites Model (Based on Filtration Theory, Chemical Nonequilbrium)
- ○ 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
- 0 Absolute Concentration Tolerance
- 0 Relative Concentratin Tolerance
- 1 Maximum Number of Iteration

☑ Use Tortuosity Factor

Number of Solutes: 3

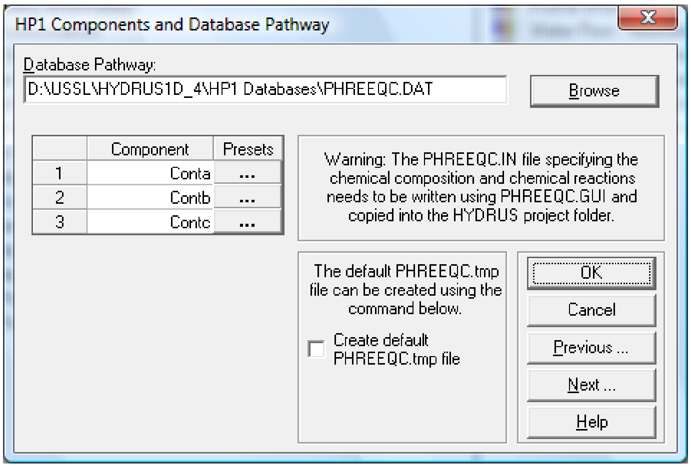
Pulse Duration: 100

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

	Component	Presets
1	Conta	...
2	Contb	...
3	Contc	...

Warning: The PHREEQC.IN file specifying the chemical composition and chemical reactions needs to be written using PHREEQC.GUI and copied into the HYDRUS project folder.

The default PHREEQC.tmp file can be created using the command below.

☐ Create default PHREEQC.tmp file

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/cm^3**

Disp.: **1 cm**

Difus. W. /diffusion coefficient in free water/: **0 cm^2/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/cm^3*). 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

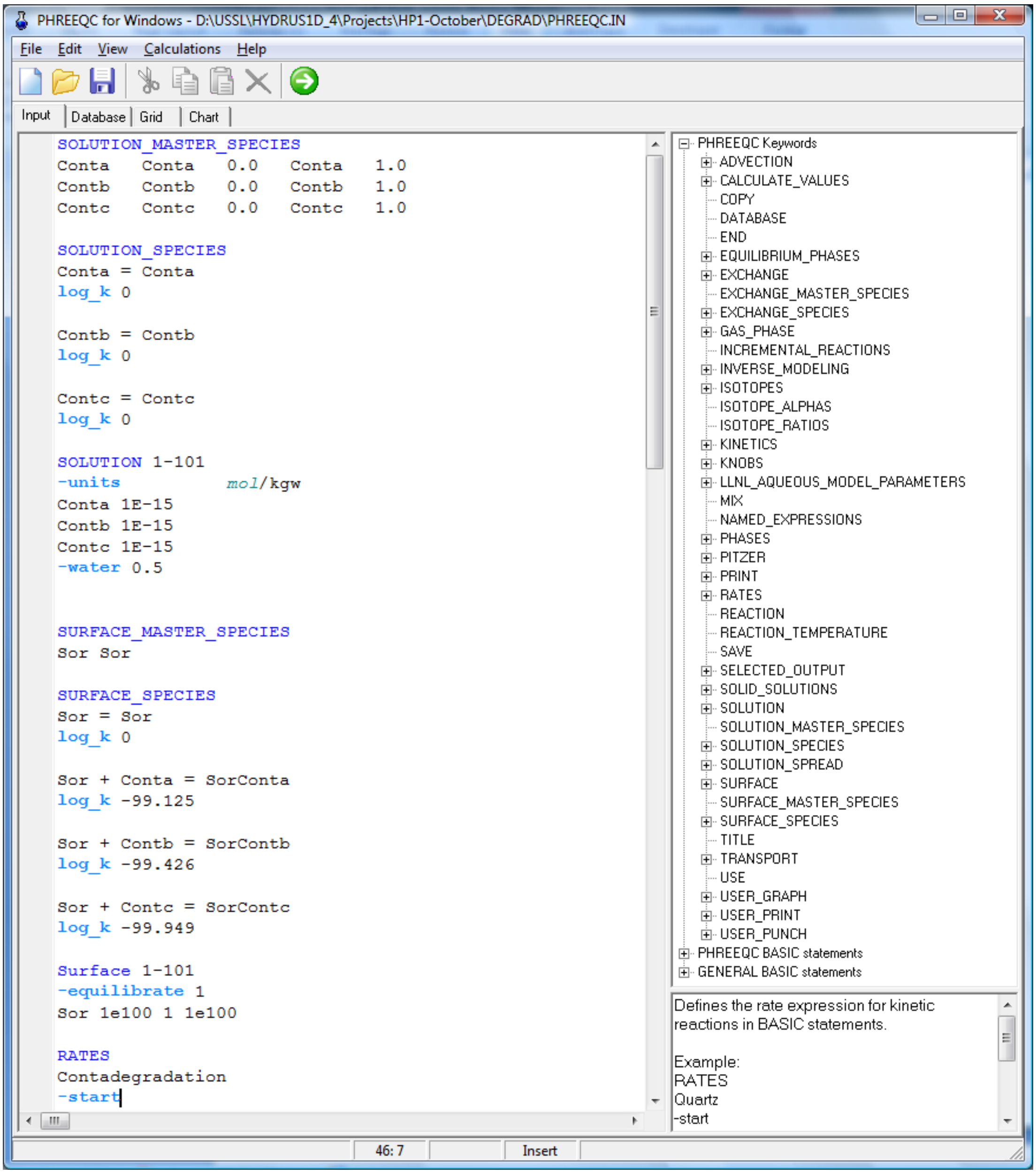
Soil Profile - Summary

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:

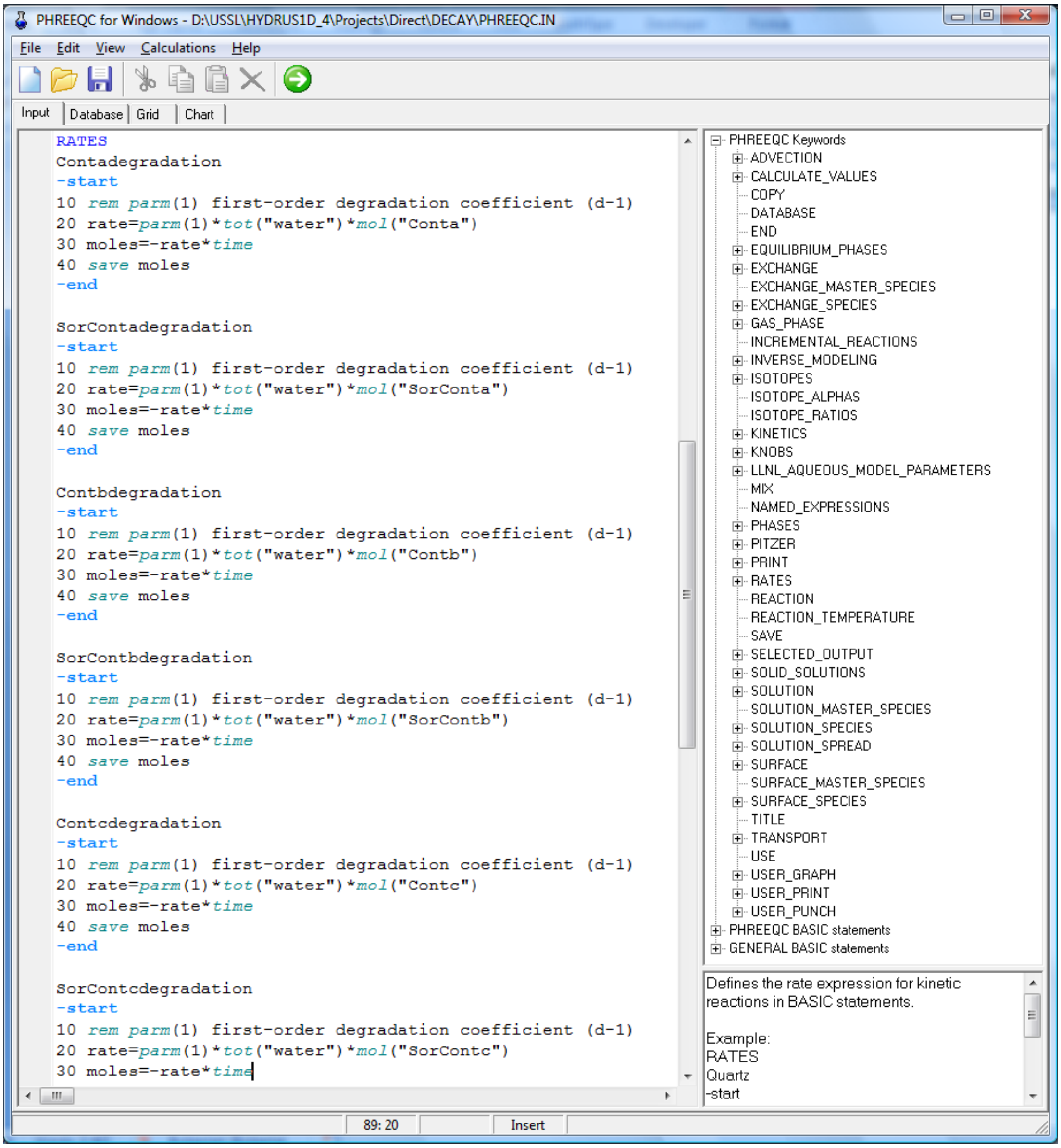


```
SOLUTION_MASTER_SPECIES
Conta    Conta    0.0    Conta    1.0
Contb    Contb    0.0    Contb    1.0
Contc    Contc    0.0    Contc    1.0

SOLUTION_SPECIES
Conta = Conta
log_k 0

Contb = Contb
log_k 0

Contc = Contc
log_k 0

SOLUTION 1-101
-units           mol/kgw
Conta 1E-15
Contb 1E-15
Contc 1E-15
-water 0.5


SURFACE_MASTER_SPECIES
Sor Sor

SURFACE_SPECIES
Sor = Sor
log_k 0

Sor + Conta = SorConta
log_k -99.125

Sor + Contb = SorContb
log_k -99.426

Sor + Contc = SorContc
log_k -99.949

Surface 1-101
-equilibrate 1
Sor 1e100 1 1e100

RATES
Contadegradation
-start
```

Defines the rate expression for kinetic reactions in BASIC statements.

Example:
RATES
Quartz
-start

and

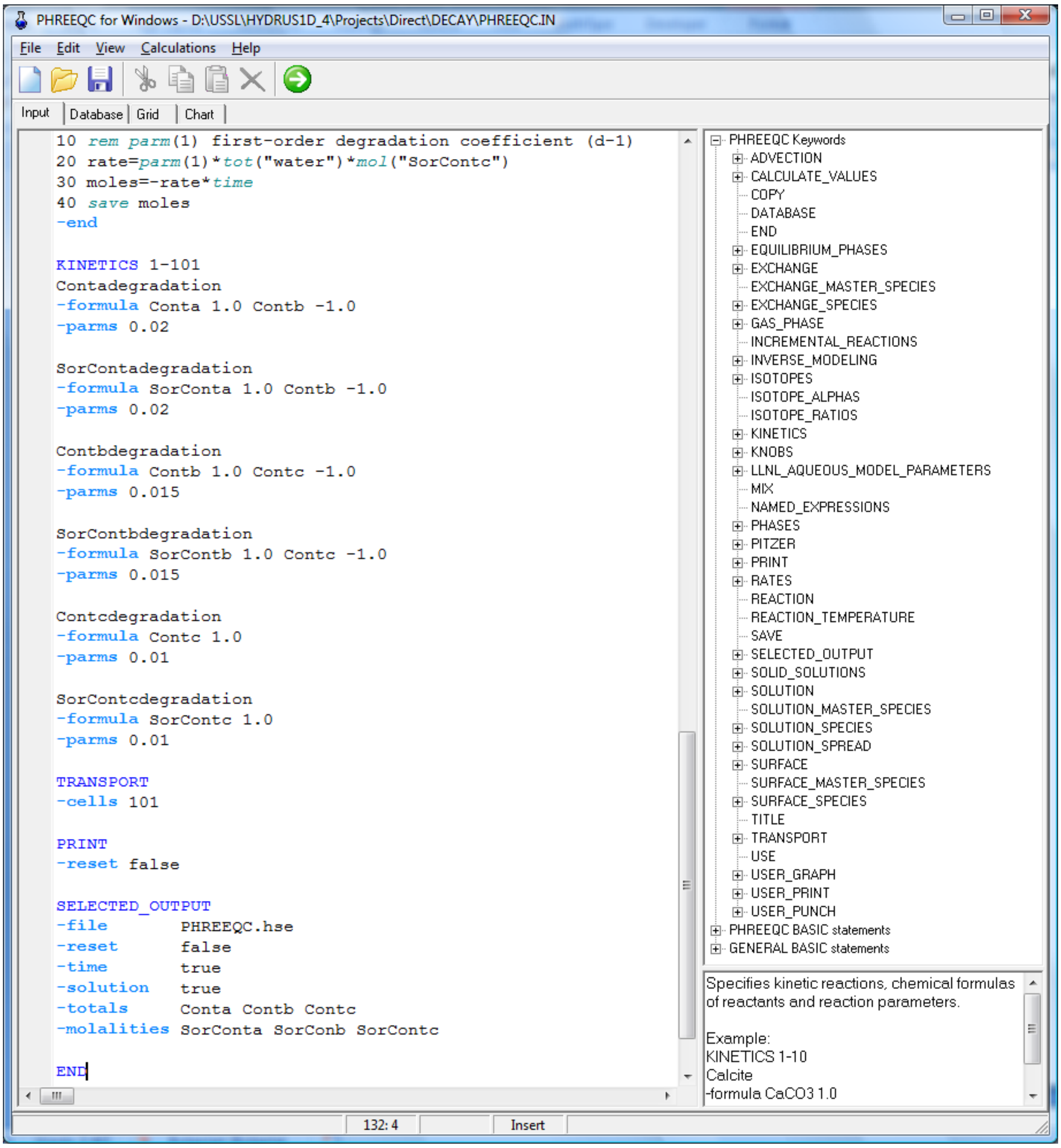


```
RATES
Contadegradation
-start
10 rem parm(1) first-order degradation coefficient (d-1)
20 rate=parm(1)*tot("water")*mol("Conta")
30 moles=-rate*time
40 save moles
-end

SorContadegradation
-start
10 rem parm(1) first-order degradation coefficient (d-1)
20 rate=parm(1)*tot("water")*mol("SorConta")
30 moles=-rate*time
40 save moles
-end

Contbdegradation
-start
10 rem parm(1) first-order degradation coefficient (d-1)
20 rate=parm(1)*tot("water")*mol("Contb")
30 moles=-rate*time
40 save moles
-end

SorContbdegradation
-start
10 rem parm(1) first-order degradation coefficient (d-1)
20 rate=parm(1)*tot("water")*mol("SorContb")
30 moles=-rate*time
40 save moles
-end

Contcdegradation
-start
10 rem parm(1) first-order degradation coefficient (d-1)
20 rate=parm(1)*tot("water")*mol("Contc")
30 moles=-rate*time
40 save moles
-end

SorContcdegradation
-start
10 rem parm(1) first-order degradation coefficient (d-1)
20 rate=parm(1)*tot("water")*mol("SorContc")
30 moles=-rate*time
```

Defines the rate expression for kinetic reactions in BASIC statements.

Example:
RATES
Quartz
-start

and



```
10 rem parm(1) first-order degradation coefficient (d-1)
20 rate=parm(1)*tot("water")*mol("SorContc")
30 moles=-rate*time
40 save moles
-end

KINETICS 1-101
Contadegradation
-formula Conta 1.0 Contb -1.0
-parms 0.02

SorContadegradation
-formula SorConta 1.0 Contb -1.0
-parms 0.02

Contbdegradation
-formula Contb 1.0 Contc -1.0
-parms 0.015

SorContbdegradation
-formula SorContb 1.0 Contc -1.0
-parms 0.015

Contcdegradation
-formula Contc 1.0
-parms 0.01

SorContcdegradation
-formula SorContc 1.0
-parms 0.01

TRANSPORT
-cells 101

PRINT
-reset false

SELECTED_OUTPUT
-file        PHREEQC.hse
-reset       false
-time        true
-solution    true
-totals      Conta Contb Contc
-molalities SorConta SorConb SorContc

END
```

Specifies kinetic reactions, chemical formulas of reactants and reaction parameters.

```
Example:
KINETICS 1-10
Calcite
-formula CaCO3 1.0
```

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 (*this is the name from the listbox*), master species (*formula for the master species, including its charge*), 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.
Conta = Conta	Association reaction for aqueous species. The defined species 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***).*
Contb = Contb	Association reaction for aqueous species. The defined species 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***).*
Contc = Contc	Association reaction for aqueous species. The defined species 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***).*
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*).
Conta 1e-15 Contb 1e-15 Contc 1e-15	Element list (*an element name, which must correspond to the items in the first column in SOLUTION_MASTER_SPECIES*), initial concentration (**note that** *it is recommended to enter some very small concentration instead of zero, otherwise the PHREEQC could ignore the component*).
-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 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.
Sor = Sor	Association reaction for surface species. The defined species 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).*
Sor + Conta = SorConta	Association reaction for the mass action equation for the linear adsorption (***note that*** *as we use surface complexation reaction, 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 + Contb = SorContb	Association reaction for the mass action equation for the linear adsorption process.
log_k -99.426	*log k* (**note that** $k = K_{d2}^{w}$). $K_{d2}^{w} = K_{d,2} * \rho_b / [Sor]$
Sor + Contc = SorContc	Association reaction for the mass action equation for the linear adsorption process.
log_k -99.949	*log k* (**note that** $k = K_{d3}^{w}$). $K_{d3}^{w} = K_{d,3} * \rho_b / [Sor]$
SURFACE 1-101	This keyword is used to define the amount and composition of each surface in a surface assemblage
-equilibrate 1	Number (*"-equilibrate" indicates that the surface 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*)
Sor 1e100 1 1e100	Surface binding-site name (*name of the surface binding site*), sites (*total number of sites for this binding site, in moles*), 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"*).
RATES	This keyword data block is used to define mathematical rate expressions for kinetic reactions. **Note that** general rate 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 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 *rem parm*(1) first-order degradation coefficient (d-1)	*numbered BASIC statement* – ***rem*** is only a comment (without effect on the calculations) indicating the meaning of the first parameter, which is first-order degradation coefficient
20 rate=*parm*(1)**tot*("water")**mol*("Conta")	*numbered BASIC statement* – **rate** defines the rate of degradation in the liquid phase, *parm*(1) is the first-order rate constant, *tot*("water") and *mol*("Conta") are the amounts of water and solute concentration in the cell.
30 moles=-rate**time*	*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*
-end	Identifier marks the end of the BASIC program by which the number of moles of a reaction for a time subinterval is calculated. Note the hyphen is required to avoid a conflict with the keyword END.
SorContadegradation	*name of rate expression* – alphanumeric character string that identifies the rate expression. In this case, it represents the degradation of the solid (adsorbed) phase of the component.
-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 *rem parm*(1) first-order degradation coefficient (d-1)	*numbered BASIC statement* – ***rem*** is only a comment (without effect on the calculations) indicating the meaning of the first parameter, which is first-order degradation coefficient
20 rate=*parm*(1)**tot*("water")**mol*("SorConta")	*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 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.
30 moles=-rate**time*	*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*
-end	Identifier marks the end of the BASIC program by which the number of moles of a reaction for a time subinterval is 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**time*	*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**time*	*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**time*	*the same as for the SorContadegradation data block*
40 *save* moles	*the same as for the SorContadegradation 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.
Contadegradation	*name of rate expression*. The rate name must correspond to the RATES data block
-formula Conta 1 Contb -1.0	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 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 *Contb* appears.
-parms 0.02	*list of parameters* –defining parameters in the rate expression, **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
-formula SorConta 1 Contb -1.0	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 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 *Contb* represents the mole transfer coefficient and the sign is negative which means *Contb* appears.
-parms 0.02	*list of parameters* –defining parameters in the rate expression, **note that** the dimension of the parameter (day^{-1}) is defined in the HYDRUS *Time Information* window.

Contbdegradation	*name of rate expression*. The rate name must correspond to the RATES data block
-formula Contb 1 Contc -1.0	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 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.
-parms 0.015	*list of parameters* –defining parameters in the rate expression, **note that** the dimension of the parameter (day^{-1}) is defined in the HYDRUS *Time Information* window.
SorContbdegradation	*name of rate expression*. The rate name must correspond to the RATES data block
-formula SorContb 1 Contc -1.0	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 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 *Contc* represents the mole transfer coefficient and the sign is negative which means *Contc* appears.
-parms 0.015	*list of parameters* –defining parameters in the rate expression, **note that** the dimension of the parameter (day^{-1}) is defined in the HYDRUS *Time Information* window.
Contcdegradation	*name of rate expression*. The rate name must correspond to the RATES data block
-formula Contc 1	Chemical formula or the name of the phase to be added by the 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).
-parms 0.010	*list of parameters* –defining parameters in the rate expression, **note that** the dimension of the parameter (day^{-1}) is defined in the HYDRUS *Time Information* window.
SorContcdegradation	*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).
-parms 0.01	*list of parameters* –defining parameters in the rate expression, **note that** the dimension of the parameter (day^{-1}) is defined in the HYDRUS *Time Information* window.
TRANSPORT	This key data block is used to simulate 1D transport processes. However, 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.
-reset false	Changes all print options (identifiers) listed on lines 2 through 15 to **true** or **false** (see 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.
SELECTED_OUTPUT	This keyword data block is used to produce a file***** that is suitable for processing by spreadsheets and other data-management software.
-file PHREEQC.hse	"-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 extensions "**.hse*", "**.out*", or "**.sel*".
-reset false	Change print options for all identifiers from line 6 to line 20 (*if 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 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 Conta Contb Contc	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 SorConta SorContb SorContc	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.

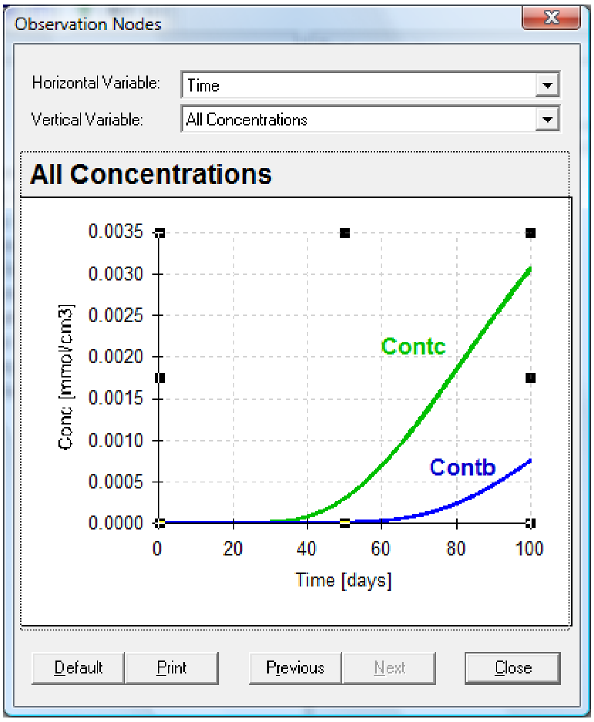
When the program finishes, open the DEGRAD folder:

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

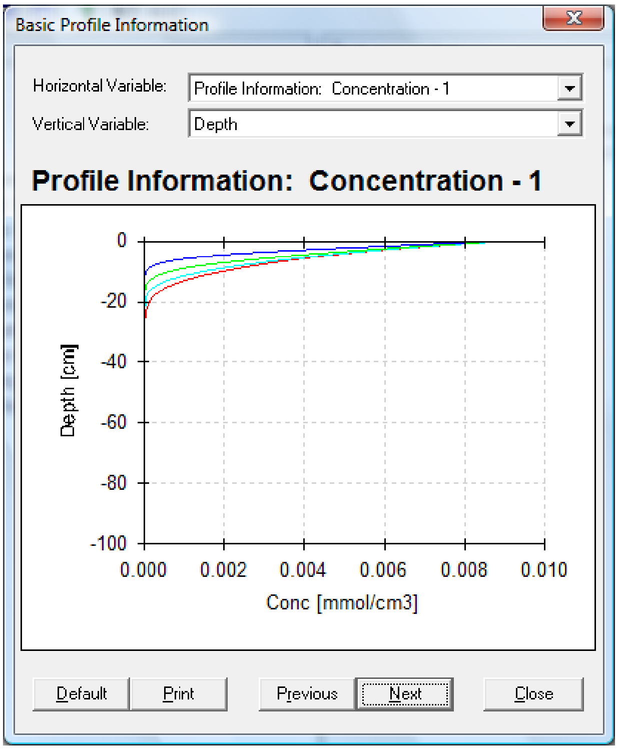


Horizontal Variable: Time

Vertical Variable: All Concentrations

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

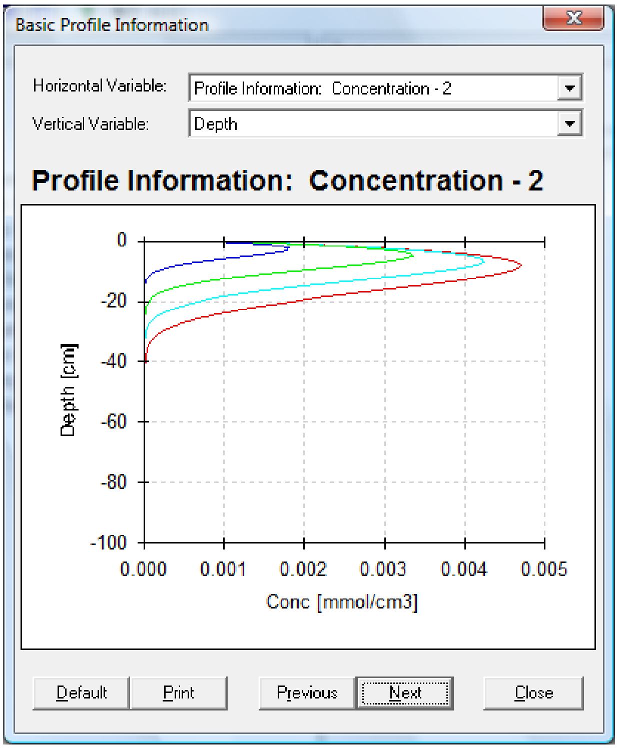


Horizontal Variable: Profile Information: Concentration - 1

Vertical Variable: Depth

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

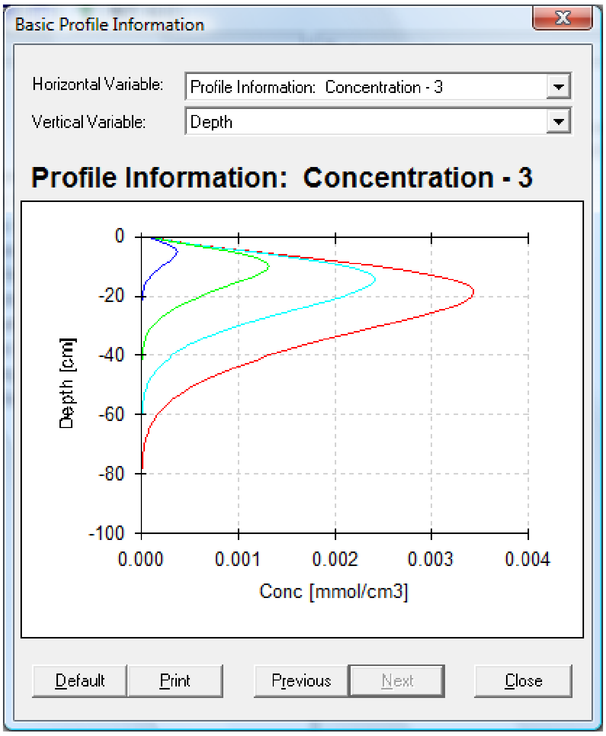


Horizontal Variable: Profile Information: Concentration - 2

Vertical Variable: Depth

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


Basic Profile Information

Horizontal Variable: Profile Information: Concentration - 3

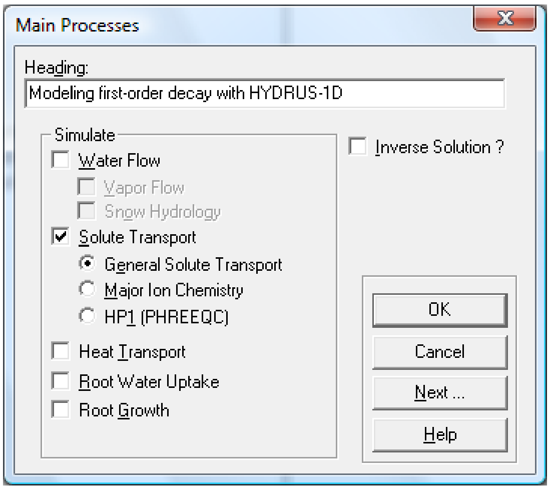
Vertical Variable: Depth

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 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

Main Process


Main Processes

Heading: Modeling first-order decay with HYDRUS-1D

Simulate
- ☐ Water Flow
  - ☐ Vapor Flow
  - ☐ Snow Hydrology
- ☑ Solute Transport
  - ● General Solute Transport
  - ○ Major Ion Chemistry
  - ○ HP1 (PHREEQC)
- ☐ Heat Transport
- ☐ Root Water Uptake
- ☐ Root Growth

☐ Inverse Solution ?

Heading: Modeling of first-order decay with HYDRUS 1D

Simulate: Solute Transport and check "General Solute Transport" option.

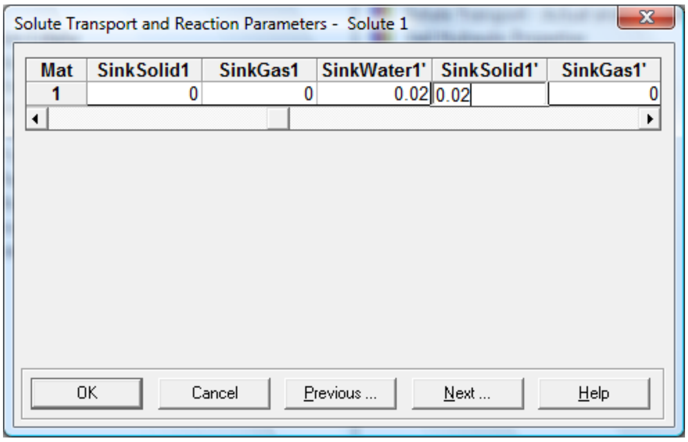
Button: "Next"

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

Time Information

Maximum Time Step: **50**

Solute Transport and Reaction Parameters – Solute 1



Solute Transport and Reaction Parameters - Solute 1

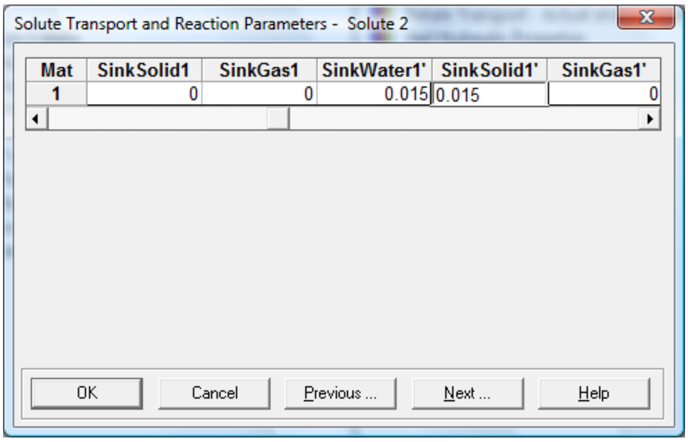
Mat	SinkSolid1	SinkGas1	SinkWater1'	SinkSolid1'	SinkGas1'
1	0	0	0.02	0.02	0

Kd: **5 g/cm^3**

SinkWater1`: **0.02 d^{-1}**

SinkSolid1`: **0.02 d^{-1}**

Solute Transport and Reaction Parameters – Solute 2



Solute Transport and Reaction Parameters - Solute 2

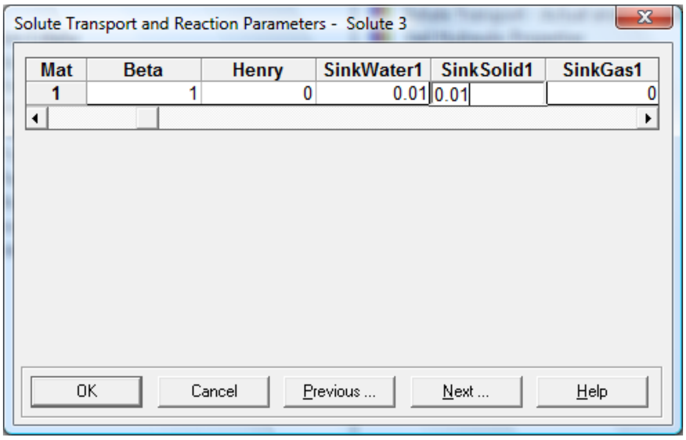
Mat	SinkSolid1	SinkGas1	SinkWater1'	SinkSolid1'	SinkGas1'
1	0	0	0.015	0.015	0

Kd: **2.5 g/cm^3**

SinkWater1`: **0.015 d^{-1}**

SinkSolid1`: **0.015 d^{-1}**

Solute Transport and Reaction Parameters – Solute 3



Solute Transport and Reaction Parameters - Solute 3

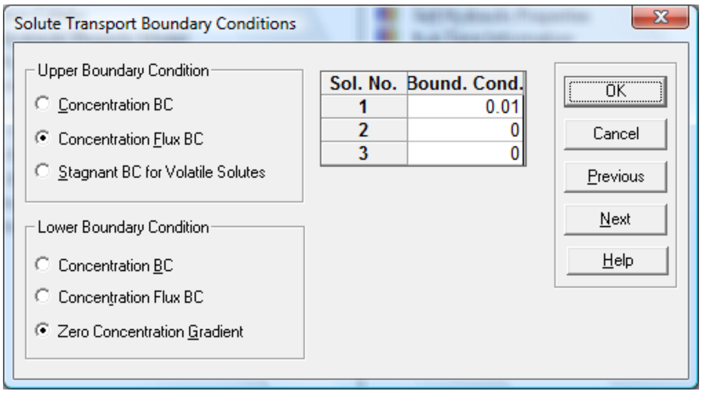
Mat	Beta	Henry	SinkWater1	SinkSolid1	SinkGas1
1	1	0	0.01	0.01	0

Kd: **0.75 g/cm^3**

SinkWater1: **0.01 d^{-1}**

SinkSolid1: **0.01 d^{-1}**

Solute Transport Boundary Conditions



Upper Boundary Condition

- ○ Concentration BC
- ● Concentration Flux BC
- ○ Stagnant BC for Volatile Solutes

Lower Boundary Condition

- ○ Concentration BC
- ○ Concentration Flux BC
- ● Zero Concentration Gradient

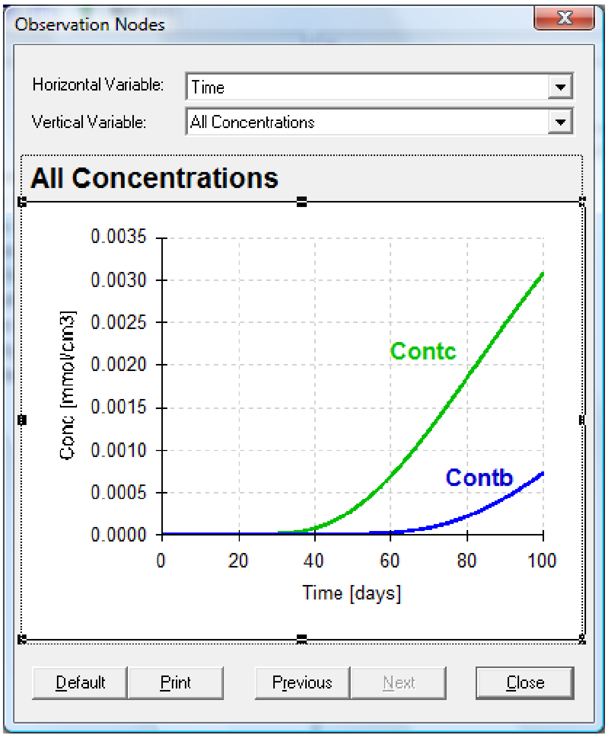
Sol. No.	Bound. Cond.
1	0.01
2	0
3	0

Bound. Cond : **0.01 mmol/cm^3**

Execute HYDRUS 1D

Post-processing

Observation Nodes

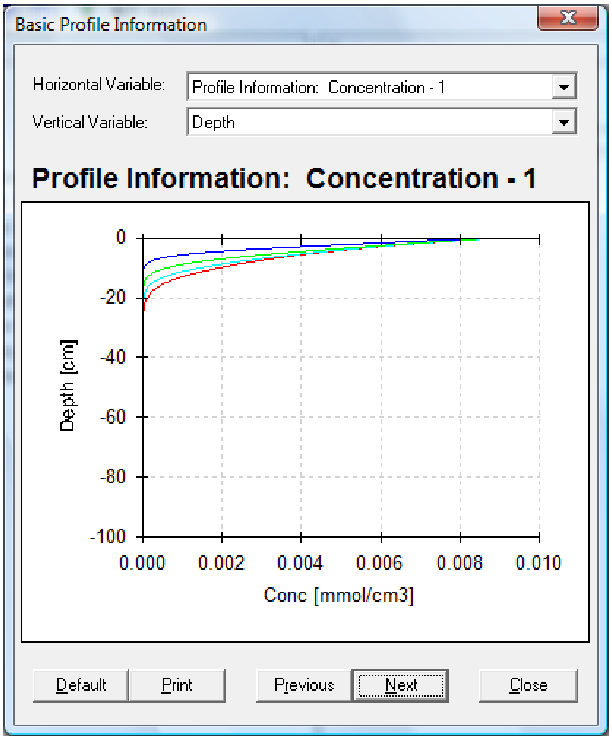


Horizontal Variable: Time

Vertical Variable: All Concentrations

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



Basic Profile Information

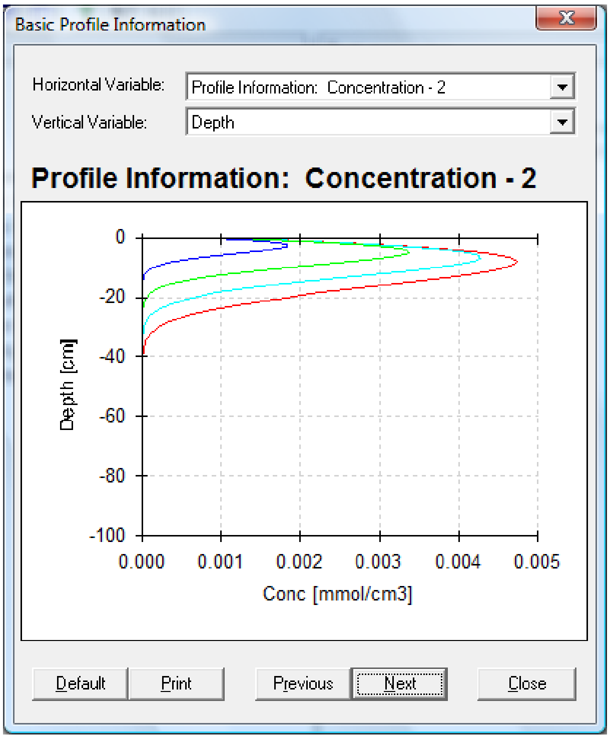
Horizontal Variable: Profile Information: Concentration - 1

Vertical Variable: Depth

Profile Information: Concentration - 1

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



Basic Profile Information

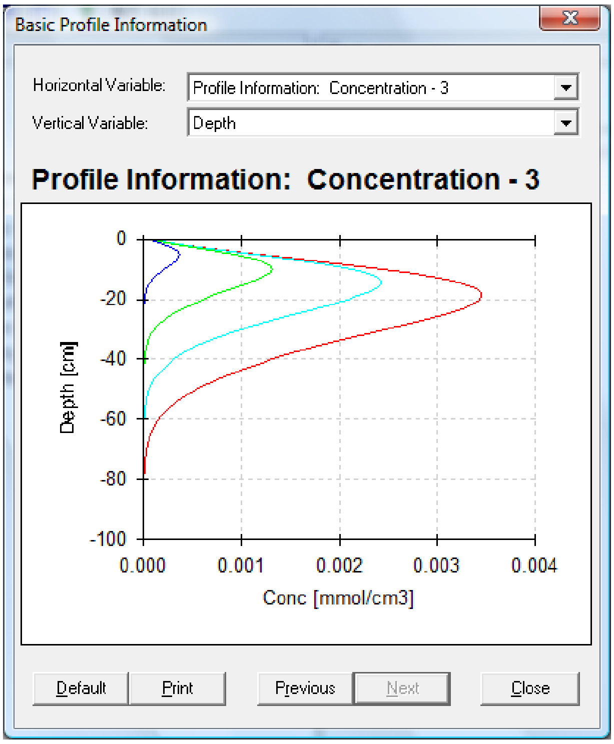
Horizontal Variable: Profile Information: Concentration - 2

Vertical Variable: Depth

Profile Information: Concentration - 2

These graphs show the *Contb* 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



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/cm^3 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/cm^3). The organic nitrogen is adsorbed with distribution coefficient $K_{d,1}$ =5.0 [cm^3/g]. Due to the *nitrification* process the organic nitrogen transforms to ammonium ion (NH_4^+) with the first-order degradation constant value of 0.02 d^{-1}, and then to nitrate ion (NO_3^-) with 0.015 d^{-1}. Finally, due to the *denitrification* process nitrate transforms to nitrogen gas (N_2) 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:

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

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

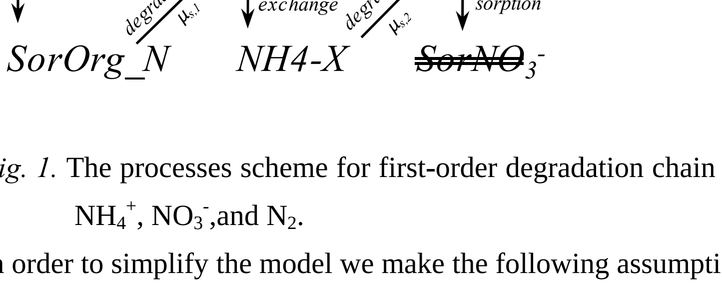


Fig. 1. The processes scheme for first-order degradation chain of linearly adsorbed component Org-N, NH_4^+, NO_3^-,and N_2.

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 [L^3M^{-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):

$$\mathrm{nNH_4^+} \quad + \quad \mathrm{Cation\text{-}X_n} \quad = \quad \mathrm{nNH4\text{-}X} \quad + \quad \mathrm{Cation^{n+}} \tag{3}$$

with equilibrium constant $$K_{NH4/Cation} = \frac{\left[\mathrm{NH4\text{-}X}\right]^{\mathrm{n}}\left[\mathrm{Cation^{n+}}\right]}{\left[\mathrm{Cation\text{-}X_n}\right]\left[\mathrm{NH4^+}\right]^{\mathrm{n}}} \tag{4}$$

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

$$\begin{aligned}\frac{\partial C_{l,Org-N}}{\partial t} = \frac{\partial}{\partial x}\left(D^w_{Org-N}\frac{\partial C_{l,Org-N}}{\partial x}\right) - \frac{q}{\theta}\frac{\partial C_{l,Org-N}}{\partial x} - \rho_b K_{d,1}\frac{\partial C_{l,Org-N}}{\partial t} \\ - \mu_{w,1}\theta C_{l,Org-N} - \mu_{s,1}\rho_b K_{d,1} C_{l,Org-N}\end{aligned} \tag{5}$$

$$\begin{aligned}\frac{\partial C_{l,NH_4}}{\partial t} = \frac{\partial}{\partial x}\left(D^w_{NH_4}\frac{\partial C_{l,NH_4}}{\partial x}\right) - \frac{q}{\theta}\frac{\partial C_{l,NH_4}}{\partial x} - \rho_b\frac{\partial C_{NH_4-X}}{\partial t} + \mu_{w,1}\theta C_{l,Org-N} \\ + \mu_{s,1}\rho_b K_{d,1} C_{l,Org-N} - \mu_{w,2}\theta C_{l,NH_4} - \mu_{s,2}\rho_b C_{NH_4-X}\end{aligned} \tag{6}$$

$$\begin{aligned}\frac{\partial C_{l,NO_3^-}}{\partial t} = \frac{\partial}{\partial x}\left(D^w_{NO_3^-}\frac{\partial C_{l,NO_3^-}}{\partial x}\right) - \frac{q}{\theta}\frac{\partial C_{l,NO_3^-}}{\partial x} + \mu_{w,2}\theta C_{l,NH_4} + \mu_{s,2}\rho_b C_{NH4-X} \\ - \mu_{w,3}\theta C_{l,NO_3^-}\end{aligned} \tag{7}$$

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

$$\frac{\partial C_{l,K}}{\partial t} = \frac{\partial}{\partial x}\left(D^w_{K}\frac{\partial C_{l,K}}{\partial x}\right) - \frac{q}{\theta}\frac{\partial C_{l,K}}{\partial x} + R_{K} \tag{9}$$

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

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., NH_4^+, Na^+, and K^+, exchange each other and the exchange reactions can be described with following equations:

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

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

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

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

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

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

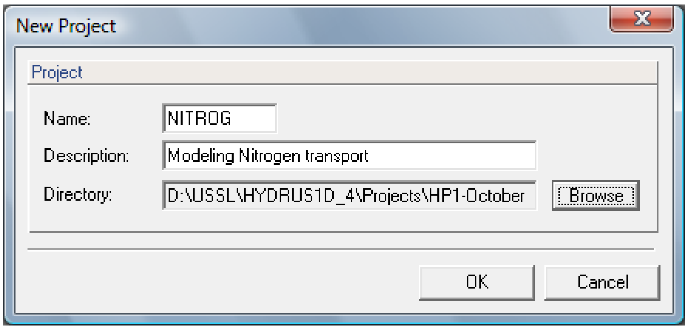
where [NH4-X], [Na-X], and [K-X] are the adsorbed concentrations, $[NH4^+]$, $[Na^+]$, and $[K^+]$ are the concentrations in the solution phase. As shown in Example 2, an additional relationship can be based on the adsorption electrical neutrality:

$[Ca\text{-}X_2] + [Na\text{-}X] + [K\text{-}X] = CEC$ (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***



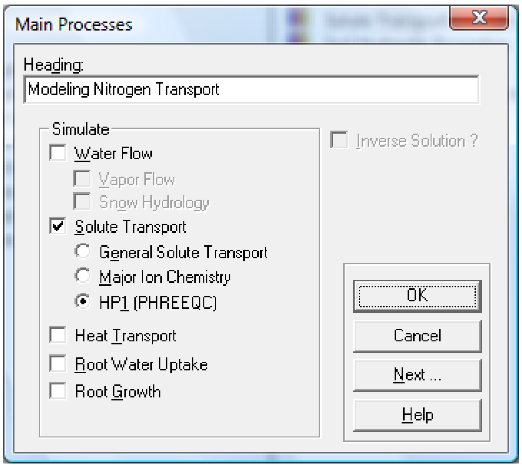
Name: NITROG
Description: Modeling Nitrogen transport
Directory: D:\USSL\HYDRUS1D_4\Projects\HP1-October

Name: NITROG

Description: Modeling Nitrogen transport

Button: "OK"

Main Processes



Heading: Modeling Nitrogen Transport

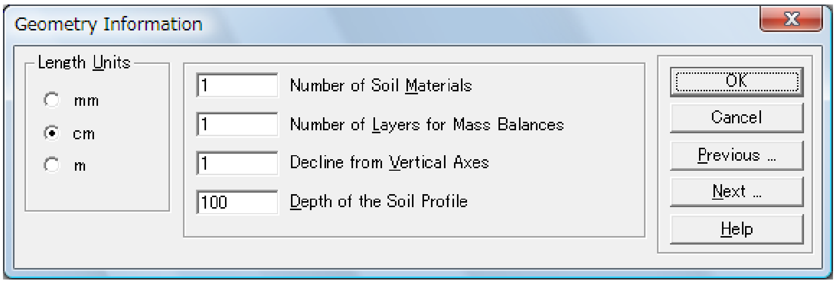
☐ Water Flow
☐ Vapor Flow
☐ Snow Hydrology
☑ Solute Transport
○ General Solute Transport
○ Major Ion Chemistry
● HP1 (PHREEQC)
☐ Heat Transport
☐ Root Water Uptake
☐ Root Growth
☐ Inverse Solution ?

Heading: Modeling Nitrogen transport

Simulate: Solute Transport and check "HP1 (PHREEQC)" option.

Button: "Next"

Geometry Information



Length Units
○ mm
● cm
○ m

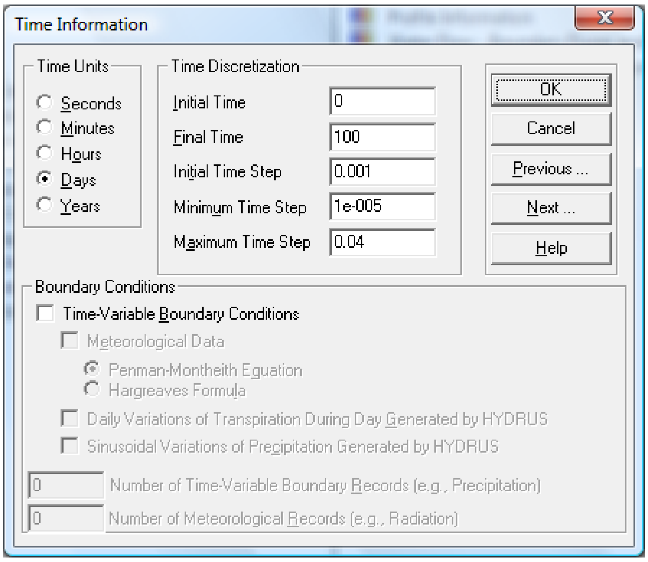
1 Number of Soil Materials
1 Number of Layers for Mass Balances
1 Decline from Vertical Axes
100 Depth of the Soil Profile

Length Units: cm

Depth of the Soil Profile: 100 cm

Button: "Next"

Time Information



Time Units
○ Seconds
○ Minutes
○ Hours
● Days
○ Years

Time Discretization
Initial Time 0
Final Time 100
Initial Time Step 0.001
Minimum Time Step 1e-005
Maximum Time Step 0.04

Boundary Conditions
☐ Time-Variable Boundary Conditions
☐ Meteorological Data
● Penman-Montheith Equation
○ Hargreaves Formula
☐ Daily Variations of Transpiration During Day Generated by HYDRUS
☐ Sinusoidal Variations of Precipitation Generated by HYDRUS
0 Number of Time-Variable Boundary Records (e.g., Precipitation)
0 Number of Meteorological Records (e.g., Radiation)

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

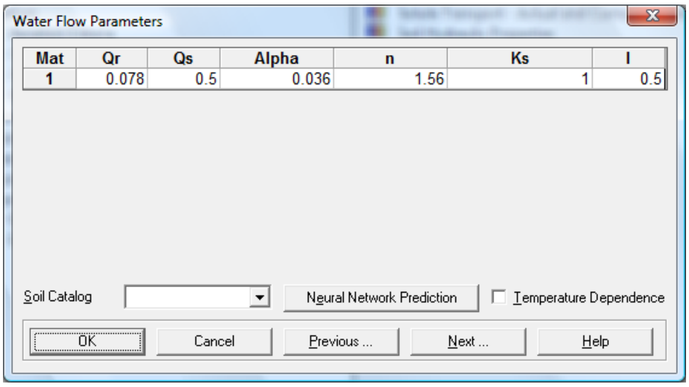
Soil Hydraulic Models

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:



Mat	Qr	Qs	Alpha	n	Ks	l
1	0.078	0.5	0.036	1.56	1	0.5

☐ Temperature Dependence

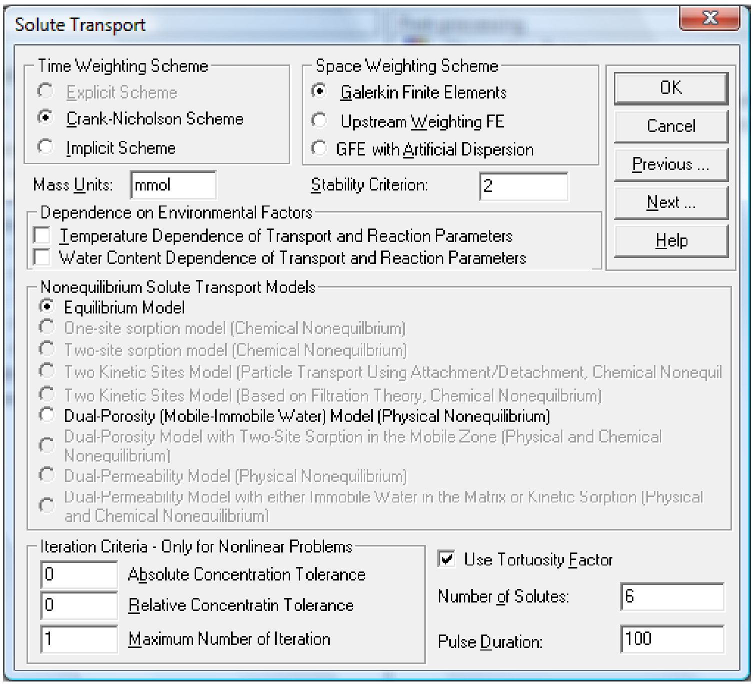
Note: In case of steady-state flow, h=0 through the profile including at the both boundaries, the "Ks" value represents the infiltrating flux.

Water Flow Boundary Condition

Upper Boundary Condition: Constant Pressure Head

Lower Boundary Condition: Constant Pressure Head

Solute Transport – General Information



Time Weighting Scheme
○ Explicit Scheme
● Crank-Nicholson Scheme
○ Implicit Scheme

Space Weighting Scheme
● Galerkin Finite Elements
○ Upstream Weighting FE
○ GFE with Artificial Dispersion

Mass Units: mmol
Stability Criterion: 2

Dependence on Environmental Factors
☐ Temperature Dependence of Transport and Reaction Parameters
☐ Water Content Dependence of Transport and Reaction Parameters

Nonequilibrium Solute Transport Models
● Equilibrium Model
○ One-site sorption model (Chemical Nonequilbrium)
○ Two-site sorption model (Chemical Nonequilbrium)
○ Two Kinetic Sites Model (Particle Transport Using Attachment/Detachment, Chemical Nonequil
○ Two Kinetic Sites Model (Based on Filtration Theory, Chemical Nonequilbrium)
○ 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
0 Absolute Concentration Tolerance
0 Relative Concentratin Tolerance
1 Maximum Number of Iteration

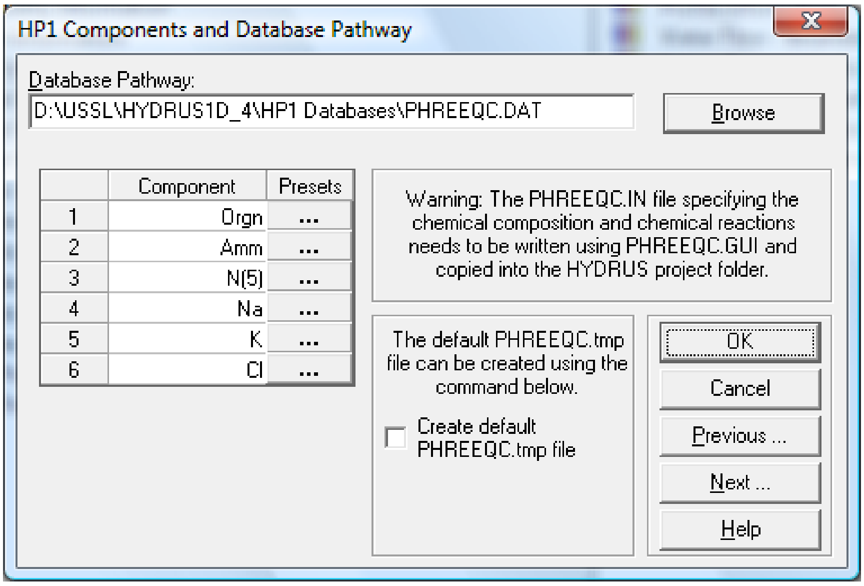
☑ Use Tortuosity Factor
Number of Solutes: 6
Pulse Duration: 100

Mass Units: **mmol**

Number of Solutes: **6**

Pulse Duration: **100**

HP1 Components and Database Pathway



Database Pathway:
D:\USSL\HYDRUS1D_4\HP1 Databases\PHREEQC.DAT

	Component	Presets
1	Orgn	...
2	Amm	...
3	N(5)	...
4	Na	...
5	K	...
6	Cl	...

Warning: The PHREEQC.IN file specifying the chemical composition and chemical reactions needs to be written using PHREEQC.GUI and copied into the HYDRUS project folder.

The default PHREEQC.tmp file can be created using the command below.

☐ Create default PHREEQC.tmp file

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/cm^3**

Disp.: **1 cm**

Difus. W. /diffusion coefficient in free water/: **0 cm^2/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

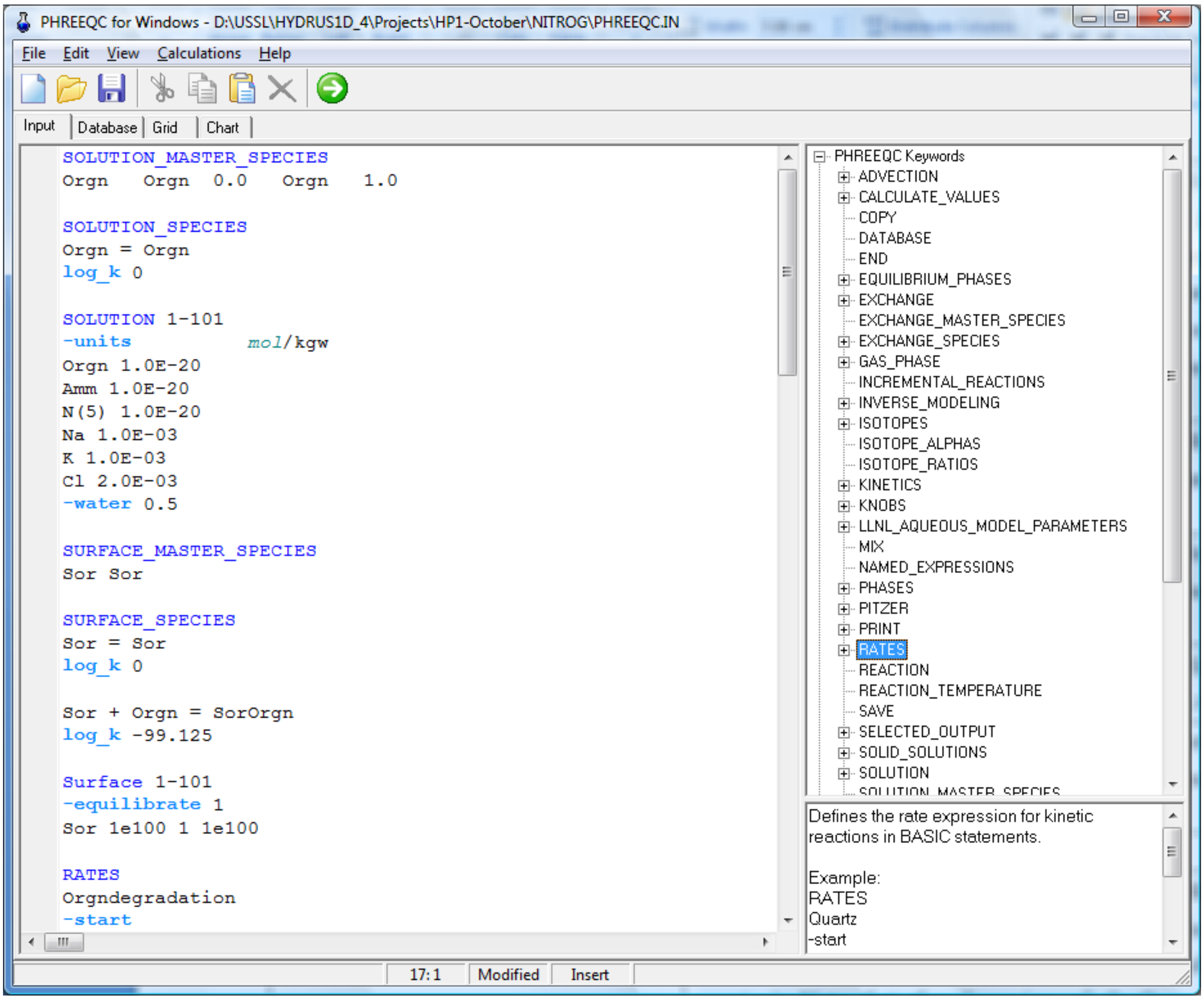
Soil Profile - Summary

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:

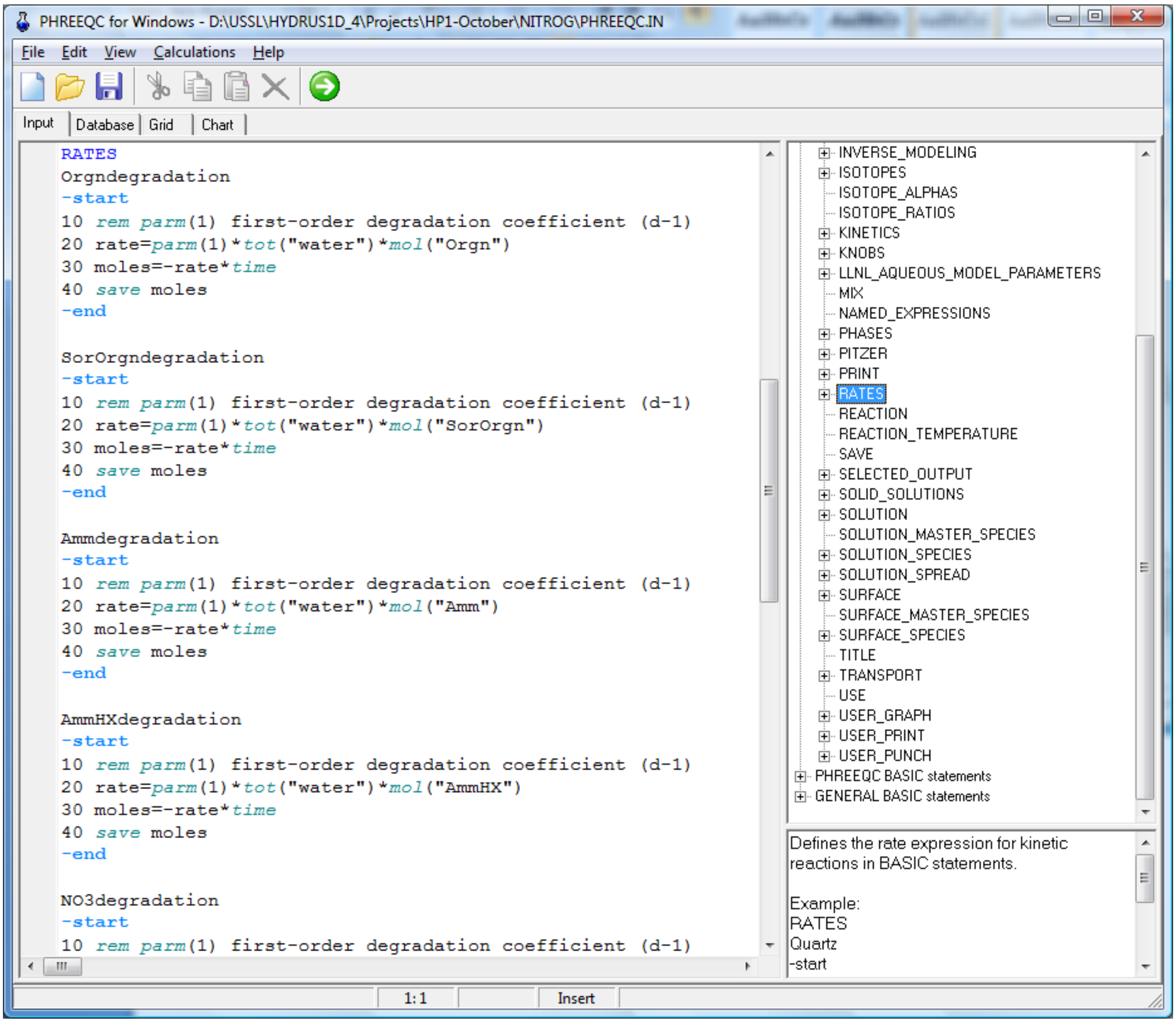


```
SOLUTION_MASTER_SPECIES
Orgn    Orgn  0.0   Orgn   1.0

SOLUTION_SPECIES
Orgn = Orgn
log_k 0

SOLUTION 1-101
-units          mol/kgw
Orgn 1.0E-20
Amm 1.0E-20
N(5) 1.0E-20
Na 1.0E-03
K 1.0E-03
Cl 2.0E-03
-water 0.5

SURFACE_MASTER_SPECIES
Sor Sor

SURFACE_SPECIES
Sor = Sor
log_k 0

Sor + Orgn = SorOrgn
log_k -99.125

Surface 1-101
-equilibrate 1
Sor 1e100 1 1e100

RATES
Orgndegradation
-start
```

Defines the rate expression for kinetic reactions in BASIC statements.

Example:
RATES
Quartz
-start

and

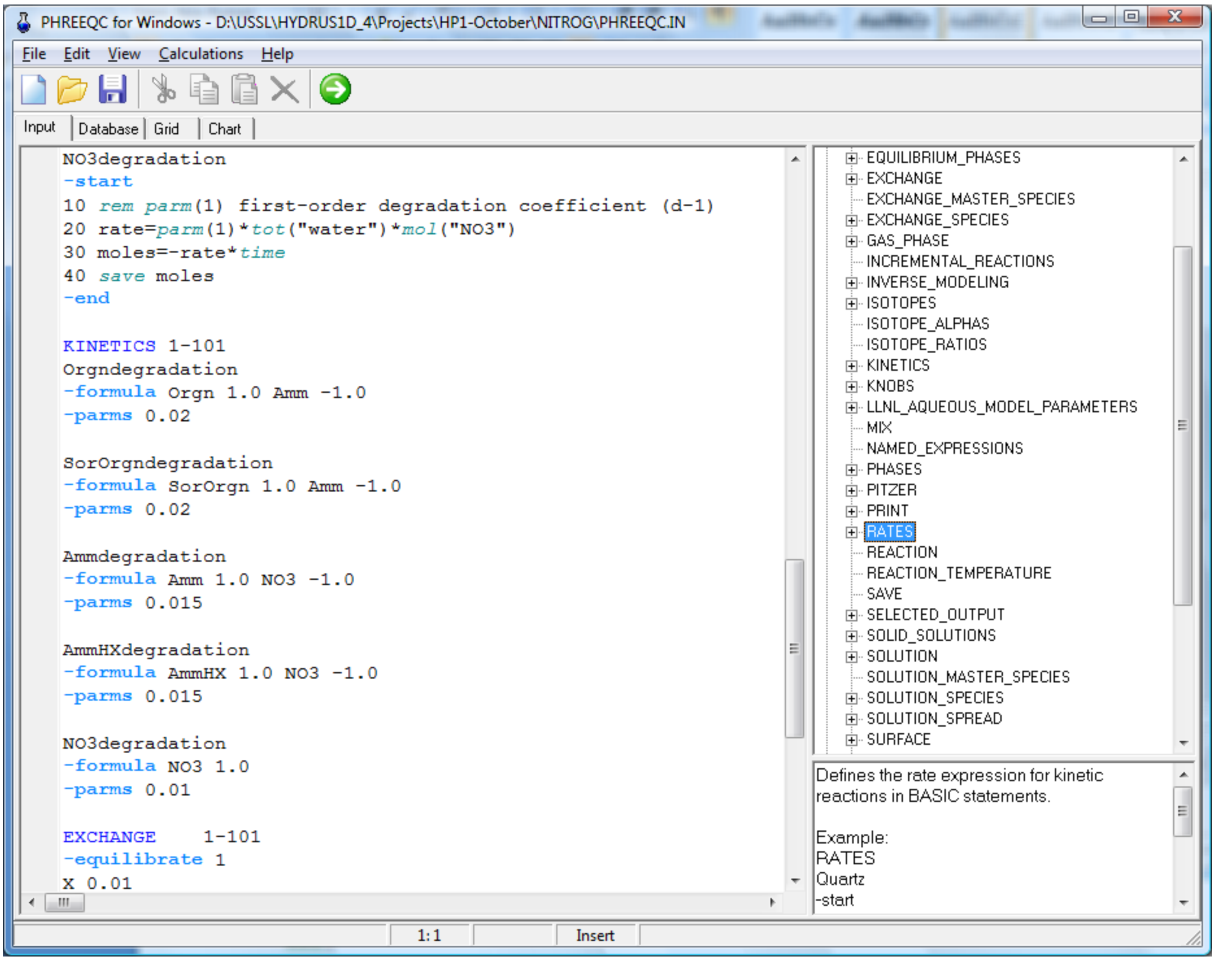


```
RATES
Orgndegradation
-start
10 rem parm(1) first-order degradation coefficient (d-1)
20 rate=parm(1)*tot("water")*mol("Orgn")
30 moles=-rate*time
40 save moles
-end

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 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
-start
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
-end

NO3degradation
-start
10 rem parm(1) first-order degradation coefficient (d-1)
```

Defines the rate expression for kinetic reactions in BASIC statements.

Example:
RATES
Quartz
-start

and

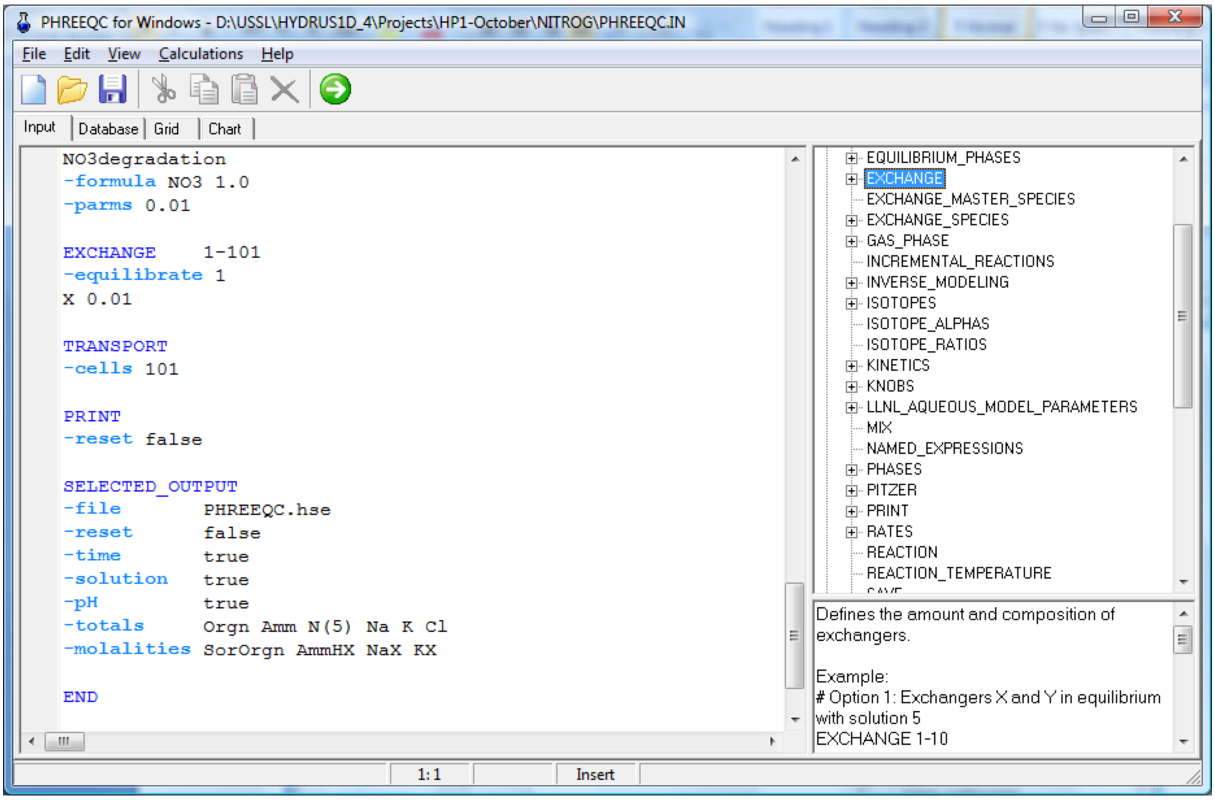


```
NO3degradation
-start
10 rem parm(1) first-order degradation coefficient (d-1)
20 rate=parm(1)*tot("water")*mol("NO3")
30 moles=-rate*time
40 save moles
-end

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

AmmHXdegradation
-formula AmmHX 1.0 NO3 -1.0
-parms 0.015

NO3degradation
-formula NO3 1.0
-parms 0.01

EXCHANGE    1-101
-equilibrate 1
X 0.01
```

Defines the rate expression for kinetic reactions in BASIC statements.

Example:
RATES
Quartz
-start

and



```
NO3degradation
-formula NO3 1.0
-parms 0.01

EXCHANGE    1-101
-equilibrate 1
X 0.01

TRANSPORT
-cells 101

PRINT
-reset false

SELECTED_OUTPUT
-file        PHREEQC.hse
-reset       false
-time        true
-solution    true
-pH          true
-totals      Orgn Amm N(5) Na K Cl
-molalities  SorOrgn AmmHX NaX KX

END
```

Defines the amount and composition of exchangers.

Example:
Option 1: Exchangers X and Y in equilibrium with solution 5
EXCHANGE 1-10

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.
Orgn Orgn 0.0 Orgn 1.0	Element name (*this is the name from the listbox*), master species (*formula for the master species, including its charge*), 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.
Orgn = Orgn	Association reaction for aqueous species. The defined species 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****).*
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 Amm 1e-20 N(5) 1e-20 Na 1.0e-03 K 1.0e-03 Cl 2.0e-03	Element list (*an element name, which must correspond to the items in the first column in SOLUTION_MASTER_SPECIES*), initial concentration (***note that*** *it is recommended to enter some very small concentration instead of zero, otherwise the PHREEQC could ignore the component*).
-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*

	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.
Sor = Sor	Association reaction for surface species. The defined species 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).*
Sor + Orgn = SorOrgn	Association reaction for the mass action equation for the linear adsorption (***note that*** *as we use surface complexation reaction, here is the place for the reaction*). Note that the dimension of *SorOrgn* is mol/kgw.
log_k -99.125	*log k* (**note that** $k = K_{d1}^{w}$). $K_{d1}^{w} = K_{d,1} * \rho_b / [Sor]$
SURFACE 1-101	This keyword is used to define the amount and composition of each surface in a surface assemblage
-equilibrate 1	Number (*"-equilibrate" indicates that the surface 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*)
Sor 1e100 1 1e100	Surface binding-site name (*name of the surface binding site*), sites (*total number of sites for this binding site, in moles*), 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"*).
RATES	This keyword data block is used to define mathematical rate expressions for kinetic reactions. **Note that** general rate 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

	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 *rem parm*(1) first-order degradation coefficient (d-1)	*numbered BASIC statement* – ***rem*** is only a comment (without effect on the calculations) indicating the meaning of the first parameter, which is first-order degradation coefficient
20 rate=parm(1)*tot("water")*mol("Orgn")	*numbered BASIC statement* – **rate** defines the rate of degradation in the liquid phase, *parm*(1) is the first-order rate constant, *tot*("water") and *mol*("Orgn") are the amounts of water and solute concentration in the cell.
30 moles=-rate*time	*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*
-end	Identifier marks the end of the BASIC program by which the number of moles of a reaction for a time subinterval is calculated. Note the hyphen is required to avoid a conflict with the keyword END.
SorOrgndegradation	*name of rate expression* – alphanumeric character string that identifies the rate expression. In this case, it represents the degradation of the solid (adsorbed) phase of the component.
-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 *rem parm*(1) first-order degradation coefficient (d-1)	*numbered BASIC statement* – ***rem*** is only a comment (without effect on the calculations) indicating the meaning of the first parameter, which is first-order degradation coefficient
20 rate=parm(1)*tot("water")*mol("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**time*	*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*
-end	Identifier marks the end of the BASIC program by which the number of moles of a reaction for a time subinterval is 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 coefficient (d-1)	*the same as for the Orgndegradation data block*
20 rate=*parm*(1)**tot*("water")**mol*("Amm")	*the same as for the Orgndegradation data block*
30 moles=-rate**time*	*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 coefficient (d-1)	*the same as for the SorOrgndegradation data block*
20 rate=*parm*(1)**tot*("water")**mol*("AmmHX")	*the same as for the SorOrgndegradation data block*
30 moles=-rate**time*	*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 coefficient (d-1)	*the same as for the Orgndegradation data block*
20 rate=*parm*(1)**tot*("water")**mol*("NO3")	*the same as for the Orgndegradation data block*
30 moles=-rate**time*	*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.
Orgndegradation	*name of rate expression*. The rate name must correspond to the RATES data block
-formula Orgn 1 Amm -1.0	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 *Amm* represents the mole transfer coefficient and the sign is negative which means *Amm* appears.
-parms 0.02	*list of parameters* –defining parameters in the rate expression, **note that** the dimension of the parameter (day^{-1}) is defined in the HYDRUS *Time Information* window.
SorOrgndegradation	*name of rate expression*. The rate name must correspond to the RATES data block
-formula SorOrgn 1 Amm -1.0	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 *Amm* represents the mole transfer coefficient and the sign is negative which means *Amm* appears.
-parms 0.02	*list of parameters* –defining parameters in the rate expression, **note that** the dimension of the parameter (day^{-1}) is defined in the HYDRUS *Time Information* window.
Ammdegradation	*name of rate expression*. The rate name must correspond to the RATES data block
-formula Amm 1 NO3 -1.0	Chemical formula or the name of the phase to be added by the kinetic reaction, **Amm**; 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”** represents the mole transfer coefficient.
-parms 0.015	*list of parameters* –defining parameters in the rate expression, **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
-formula AmmHX 1 NO3 -1.0	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 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.
-parms 0.015	*list of parameters* –defining parameters in the rate expression, **note that** the dimension of the parameter (day^{-1}) is defined in the HYDRUS *Time Information* window.
NO3degradation	*name of rate expression*. The rate name must correspond to the RATES data block
-formula NO3 1	Chemical formula or the name of the phase to be added by the 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).
-parms 0.010	*list of parameters* –defining parameters in the rate expression, **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).
X 0.01	Exchange site (only the name of the exchange site needs to be entered), amount (quantity of exchange site, in moles). Note that the dimension is by default always in moles. This means that every cell possesses 0.01 mol of the exchanger.
TRANSPORT	This key data block is used to simulate 1D transport processes. However, 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.
-reset false	Changes all print options (identifiers) listed on lines 2 through 15 to **true** or **false** (see 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.
SELECTED_OUTPUT	This keyword data block is used to produce a file***** that is suitable for processing by spreadsheets and other data-management software.
-file PHREEQC.hse	"-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 extensions "**.hse*", "**.out*", or "**.sel*".
-reset false	Change print options for all identifiers from line 6 to line 20 (*if 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 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.

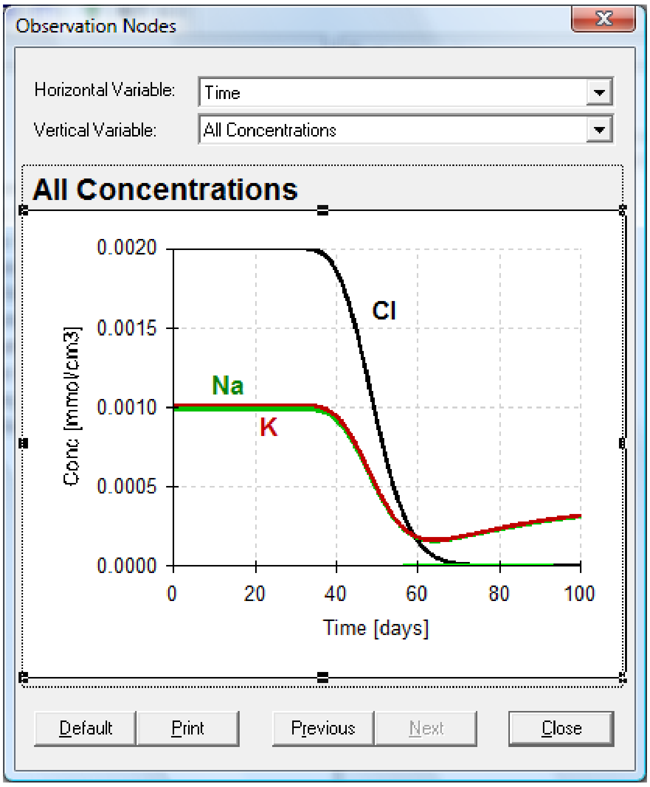
Go back to HYDRUS-1D GUI and execute HP1.
When the program finishes, open the NITROG folder:

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

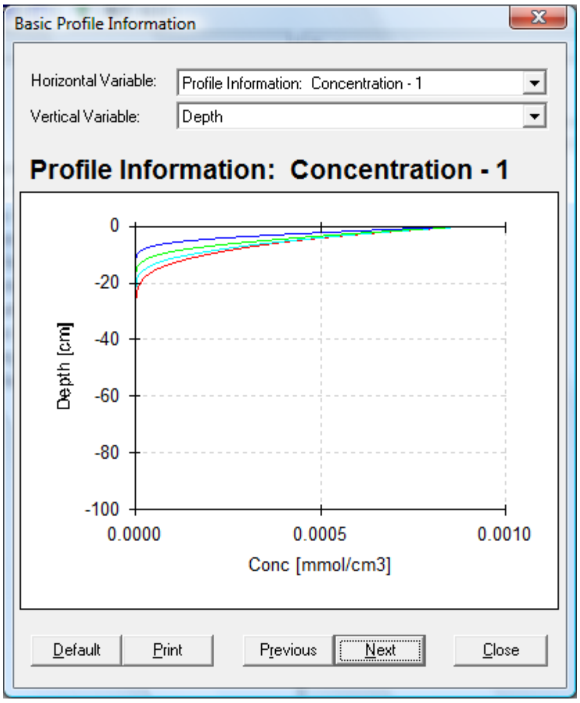


Horizontal Variable: Time

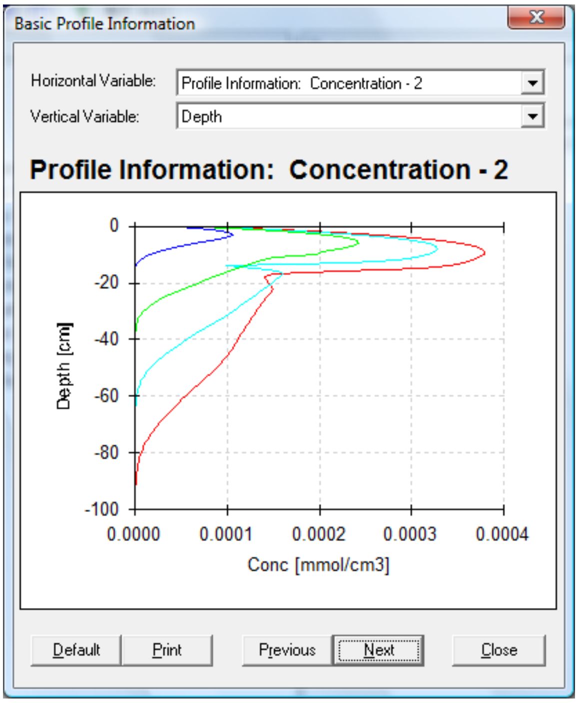
Vertical Variable: All Concentrations

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


Horizontal Variable: Profile Information: Concentration - 1

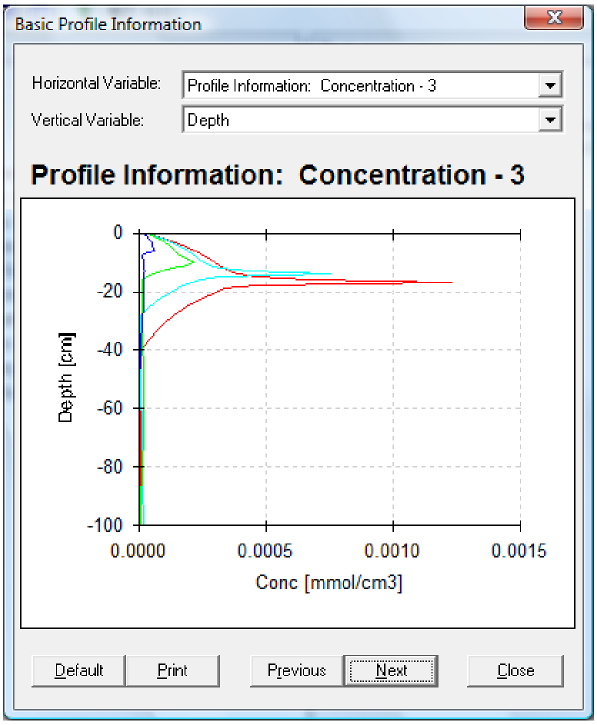
Vertical Variable: Depth


Horizontal Variable: Profile Information: Concentration - 2

Vertical Variable: Depth

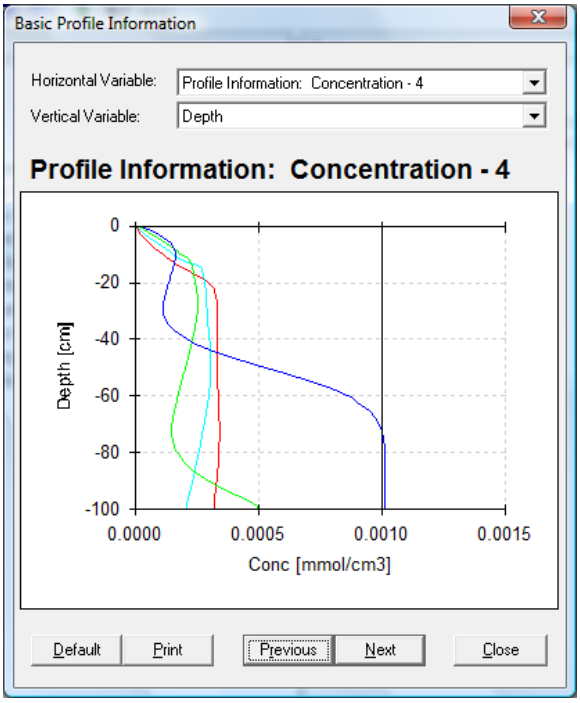
The *Orgn* concentration in the solute phase through the profile at the initial time (the black graph) and at the printed time steps.

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


Horizontal Variable: Profile Information: Concentration - 3

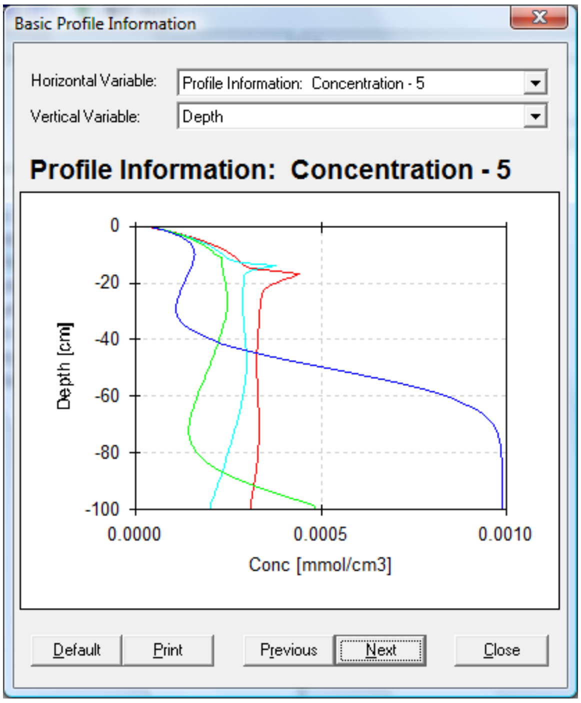
Vertical Variable: Depth

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


Horizontal Variable: Profile Information: Concentration - 4

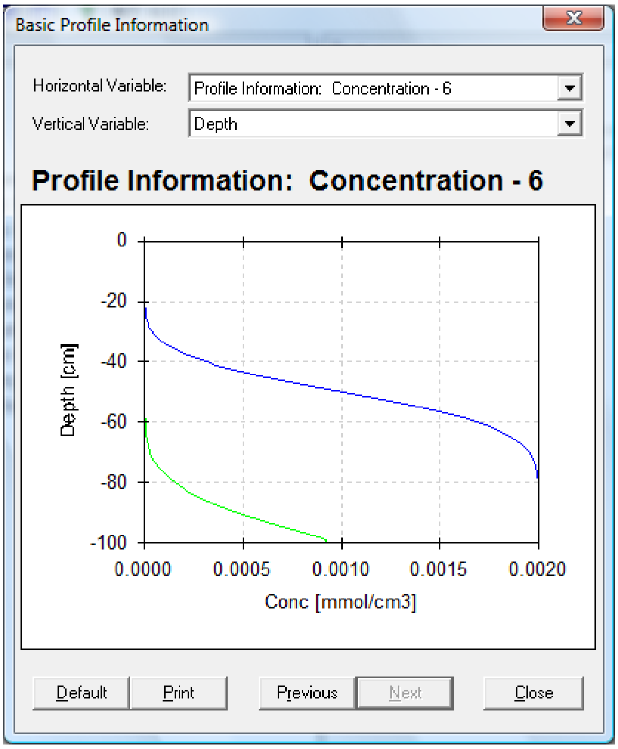
Vertical Variable: Depth

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


Horizontal Variable: Profile Information: Concentration - 5

Vertical Variable: Depth

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


Horizontal Variable: Profile Information: Concentration - 6

Vertical Variable: Depth

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

4. マルチステップ法による水分移動特性の推定

Estimation of soil hydraulic property using a multi-step method

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1. はじめに

マルチステップ法は，不飽和土の保水性，透水性を定量的に把握することを目的とし，水分保持曲線と不飽和透水係数の関数式に含まれるパラメーターを逆解析手法で決定する方法である。適用範囲は使用する実験装置に依存し，飽和から数百kPaの範囲までの広い範囲に適用できる。吸引法，土柱法，加圧板法などによる水分保持曲線，内部排水法，フラックス制御や圧力制御による定常浸潤法などによる不飽和透水係数と含水量との関係などを利用することもできる汎用的な方法である。アメリカでは標準的な方法として，Methods of Soil Analysis Part4 - Physical Methods (Hopmans ら，2002)に記述されている。Gardner (1956)の加圧板流出法，Doering (1965)のワンステップ加圧流出法，Kool ら(1985)のワンステップ流出法，Eching and Hopmans (1993)のマルチステップ加圧流出法，van Dam ら(1994)のマルチステップ加圧流出法，Inoue ら(1998)のマルチステップ吸引抽出法，Fujimakiら(2004)の浸潤過程のマルチステップ流入法など，研究の展開がなされた。また，Kosugi and Inoue (2002)やDurnerら(2007)は成層の問題にも逆解析法を適用して土壌の水分移動特性を推定している。特に，不撹乱土壌に対して，水分移動特性値（水分特性曲線・不飽和透水係数）を短期間（10日程度以内）に決定できるマルチステップ法は有効な試験法として特記できる。ここでは，筆者が経験したマルチステップ法と，その問題を解説し，最新のHYDRUS-1D（フリーソフト）を用いて，簡単な演習を試みる。

2. 装置と試験

2.1 試験装置

マルチステップ流出法の装置は，定常法，準定常法，非定常法に使用できる。加圧条件下で空気が容器内から漏出しないように，ドーナツ型ステンレス板を用いて，圧力容器の機密性が改良された（井上，1996，1997；森ら，2001）。非定常法については，テンシオメーターによる圧力水頭と流出量の経時変化に対して，van Genuchten式のパラメーターを逆解析によって求める方法が普及している。図-1に代表的な試験装置を示す。流出量の計測は，

ビューレットによる目視記録法，圧力センサーによる水位自記法，電子天秤による流出重量自記法などがある。

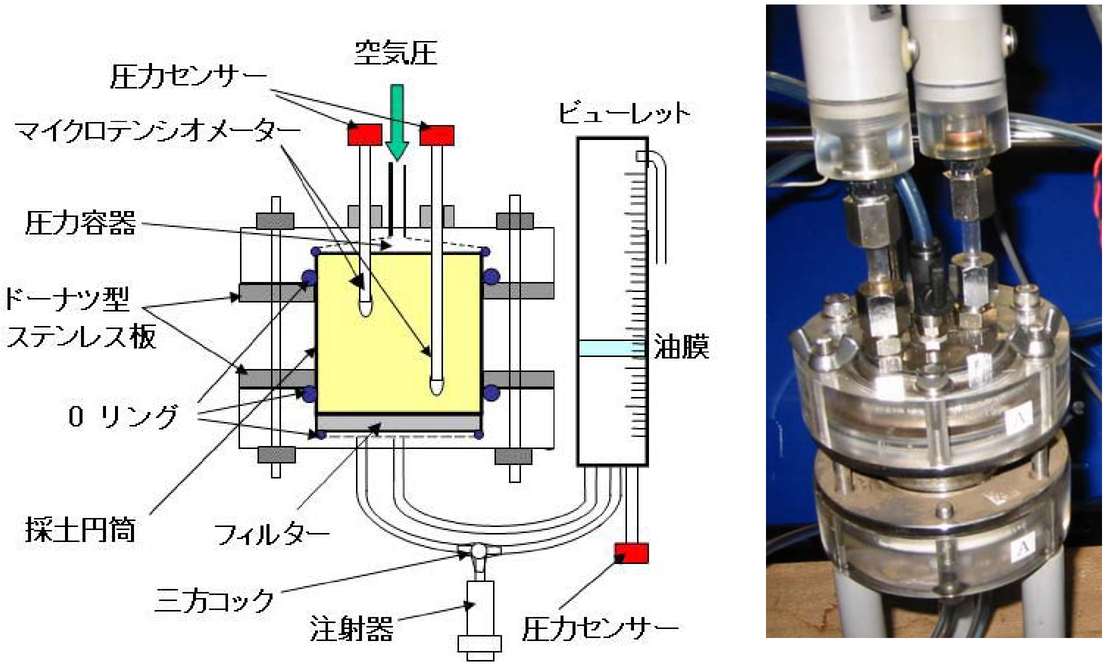

図-1　マルチステップ流出法の試験装置

2.2 試験手順

現場から定容積採土法等によって不撹乱状態で土壌を採取する。採土円筒は，内径50mm，高さ51mmの容積（V）100cm^{3}の容器，あるいは，内径84.6mm，高さ64mmの容積（V）360cm^{3}の容器など種々の大きさがあり，定容積採土法と同じ容器を使用する。フィルターには，100kPa用ハイフローセラミックフィルター（砂質土では焼結ガラスフィルター）を用い，試験の前後にフィルターの飽和透水係数を求める。

測定の手順として，まず圧力容器から加圧空気が漏れないことを確認する。フィルターを脱気飽和させ，不撹乱土を試験装置にセットする。このとき，上下端を試料受器ではさみ込み，Oリングとドーナツ型ステンレス板で密閉する。上部試料受器にマリオットタンク（水位一定装置）を接続する。ビューレットに水を入れ下部試料受器から供試体を飽和させる。フィルター部下端の空間に気泡があれば，注射器と三方コックを用いて一方向の水流を発生させて気泡をビューレットに導く。ビューレットからオーバーフローした流出量あるいはマリオットタンクによる給水量，圧力容器の中に2本のテンシオメーターを異なる深さに挿入して供試体の動水勾配を測定し，定常浸潤法により土の飽和透水係数を求める。

マリオットタンクからの給水を停止して，ビューレットの自由水面の位置を採土円筒の上端位置に合わせて湛水深がゼロとなるように調節して全体の水量を測定し，後で飽和体積含

水率を推定する。自動圧力調節器を用いて，供試体上部から空気圧を段階的に加える。設定した空気圧に対して流出量がなくなり，ほぼ平衡状態とみなせる状態（準定常状態）に達したら，更に段階的に空気圧を加える。この準定常法では時間がかかるが，平衡に達する前に，次のステップに移行する非定常法を採用する。多くの土の場合，初期値を30cmH_2Oとして，段階的に60cmH_2O, 120cmH_2O, 240cmH_2O, 400cmH_2O, 600cmH_2O, 850cmH_2Oと約8時間ごとに空気圧を上昇させる。これらの値は土の種類により異なり，砂質土の場合，初期値を10cmH_2Oとして，20cmH_2O, 30cmH_2O, 40cmH_2O, 50cmH_2O, 100cmH_2Oと空気圧を上昇させる。これと同時に累積流出量（ビューレットを用いる場合には，蒸発損失を軽減させるために水面に油膜を設ける），およびテンシオメーターを用いて圧力容器内の所定の位置で圧力水頭を測定する。したがって，測定項目としては，空気圧，圧力水頭，累積流出量の経時変化を計測する。

測定終了後に供試体を取り出して炉乾燥法で実験終了時の体積含水率θ_fと乾燥密度を測定する。飽和体積含水率θ_sは，θ_fと測定したデータ累積流出量$CumQ$の経時変化から，$\theta_s = CumQ / V + \theta_f$で計算する。

準定常法による水分特性曲線は，設定した空気圧に対して測定した体積含水率θと圧力水頭h_pの関係から決定する。空気圧を一定に維持している段階の平衡状態の体積含水率θ□は，実験終了時の体積含水率θ_fと測定したデータ累積流出量$CumQ$ の経時変化から，同一時間の測定値を用いて，$\theta(t) = CumQ(t) / V + \theta_f$ で計算する。一方，圧力水頭h_p(cm)は，

$$h_p = h_\mathrm{t} - h_\mathrm{a} \tag{1}$$

で計算する。ここで，h_t :テンシオメーターで測定したポーラスカップの位置の圧力水頭(cm), h_a:供試体に加圧された空気圧（水頭換算, cmH_2O)である。

マルチステップ流出法の実験データから，いろいろな組合せで目的関数を選択して，物性値のパラメーターを決定できる。ここでは，水分特性曲線にvan Genuchtenの式，透水係数にMualem式を採用した方法を説明する。マルチステップ流出法の実験は，初期条件（$t = 0$）として

$$h_p(z,t) = h_p(\mathrm{z}) \qquad 0 < z < L \tag{2}$$

で，境界条件は，

$$q(z,t) = 0 \qquad t > 0, z = L \tag{3}$$

$$h_p(z,t) = h_\mathrm{t}(\mathrm{z,t}) - h_\mathrm{a} \qquad t > 0, z = 0 \tag{4}$$

で，一次元の水分移動方程式

$$\frac{\partial \theta}{\partial t}=\frac{d\theta}{dh_p}\frac{\partial h_p}{\partial t}=\frac{\partial}{\partial z}\left[K(h_p)\frac{\partial h_p}{\partial z}+K(h_p)\right] \qquad (5)$$

を解く。ここで，L は供試体の長さ，体積含水率θと圧力水頭h_pとの関係に，次の van Genuchten式$^{11)}$を用いる。

$$S_e(h_p)=\frac{\theta-\theta_r}{\theta_s-\theta_r}=\frac{1}{(1+\left|\alpha\, h_p\right|^n)^m} \qquad (6)$$

ここで，S_e：有効飽和度，θ_r：残留体積含水率，α：実験常数である。不飽和透水係数$k_{wu}(h_p)$の関係にはMualem式 を用いる(van Genuchten,1980)$^{11)}$。

$$k_{wu}(h_p)=k_{ws}S_e^l[1-(1-S_e^{1/m})^m]^2 \qquad (7)$$

ここで，k_{ws}：飽和透水係数，l, m, n：実験係数(m=1-1/n)である。

これらのvan Genuchten式と Mualem式を用いて数値計算を行い，実験による圧力水頭（h_p）の経時変化と累積流出量($CumQ$)の経時変化との残差が最小になるようにLevenberg－Marquardt法によって水分移動特性値のパラメーターを得る。ここで，残差としての目的関数$OF(b)$は，

$$\begin{aligned}
OF(b) &= W_Q\sum_{i=1}^{N}\{w_i[CumQ_m(t_i)-CumQ_o(t_i,b)]\}^2\\
&+W_h\sum_{i=1}^{M_1}\{v_i[h_{1m}(t_i)-h_{1o}(t_i,b)]\}^2\\
&+W_h\sum_{i=1}^{M_2}\{v_i[h_{2m}(t_i)-h_{2o}(t_i,b)]\}^2\\
&+W_j\sum_{j=1}^{L}\{u_j[\theta_m(h_j)-\theta_o(h_j,b)]\}^2\\
&+W_g\sum_{g=1}^{G}\{y_g[k_m(h_g)-k_o(h_g,b)]\}^2
\end{aligned} \qquad (8)$$

で与えられ，$CumQ$, h, θ, k はそれぞれ，累積流出量，圧力水頭，体積含水率，不飽和透水係数で，Wは無次元化係数，v, u, yは実験の重み係数，添え字mは実験値，添字oは数値実験値を意味する。また，式(8)の中に，次に示すような，いろいろな測定値を選択することが可能である。

① 累積流出量$CumQ(t)$のデータのみを用いる場合

② 試料の中心点で，圧力水頭$h_p(t)$ のデータのみを用いる場合

③ $CumQ(t)$と圧力水頭$h_p(t)$を用いる場合

④ 圧力水頭$h_{p1}(t)$と$h_{p2}(t)$を用いる場合

⑤ $CumQ(t)$と圧力水頭$h_{p1}(t)$と$h_{p2}(t)$を用いる場合

⑥ $CumQ(t)$と$h_p(t)$に加えて，準定常法の水分特性曲線$\theta(h_p)$のデータを含める場合

⑦ $CumQ\ (t)$と$h_p(t)$に加えて，別の水分特性曲線と不飽和透水係数$K(h_p)$のデータを含める場合

上記の他に，種々のデータを組み合わせて逆解析が可能である。基本的に，目的関数$OF(b)$には，累積流出量$CumQ(t)$を含める組み合わせが推奨されている。

３．問題点

3.1 試験

試験を行う上の留意点として，

① 定常浸潤法で，それぞれの含水量に対して物性値を求める定常法と比べると，実験時間が少ない（長くても，約10日間で実験終了）。

② 装置自体は，比較的簡単な構成からなり，取り扱いが容易であり，不撹乱の土壌に対して実験できる。

③ 下部フィルターの透水係数を知る必要がある。

④ テンシオメーターのデータを用いる場合，圧力水頭が-850cm程度で，測定限界になる。

⑤ 例えば，テンシオメーターを使用しないで，300kPa用のフィルターを用いる場合には，累積流出量($CumQ$)の経時変化のデータを基に，300kPaまでの特性値を決定できる。

⑥ 吸引法などの負圧実験と比べて，負圧状態での気泡の発生がないので，実験が容易である。

⑦ 土中に大きな礫を含むもの，乾燥に伴って著しく収縮する土には適用しにくい。

3.2 逆解析

マルチステップ流出法は，多くの土に対し適用され，市販のフリーソフトHYRDUS-1D(Simunekら, 2005)や，フリーソフトWASH-1D（藤巻ら, 2001）でパラメーターを推定できるがソフトの使用法を熟知する必要がある。

逆解析を行う上の留意点として，

① 試験を行った実験状況と同じ，初期条件，境界条件を与える必要がある。

② 下端フィルターの特性値の与え方に注意を要する。

③ 逆解析では，プログラムを実行して，巨視的な最小値を得るために，適当なパラメーターの初期値を決定する基礎知識が必要である。

④ ひとつの方法として，Echingら(1993)は，異なる初期値を与えて，いずれも同じ最適パラメーターになることを確認するアルゴリズムを採用しているので，参考になる。

⑤ 累積流出量(*CumQ*)の経時変化のみをデータとして使用する場合，パラメーターの初期値は極めて重要になる。1点でも，水分特性曲線$\theta(h_p)$のデータがあると逆解析が容易になる。

⑥ 入力データの累積流出量$CumQ(t)$，圧力水頭$h_{p1}(t)$と$h_{p2}(t)$などの時間変化のデータがばらつく場合は，逆解析は困難となる。

⑦ 信頼できる実験データに対して，重みをつけて逆解析することを奨励する。

3.3 まとめ

不飽和土の水分移動を定量的に把握するために，水分移動式として式(5)を採用していることが前提条件で，パラメーターの決定のために，van Genuchten式と Mualem式の代わりに，修正van Genuchten式，小杉の式，Brooks-Corey式，動水-不動水モデル式などを採用できる。実験の下端条件に圧力水頭の経時変化を境界条件に組み入れることができる。さらに，実験に合致した条件で逆解析を行うことが可能で，目的関数の中に，他の定常法で得られた物性値を加味できる特徴を有し，今後，普及する方法である。しかし，実験結果に依存するので，試験に対する経験と，逆解析を行うためのノウハウが必要で，少なくとも，論文に書かれていない苦労話は貴重な情報となる。

別紙

付録(1)： 「演習」 マルチステップ法の入力値

付録(2)： 講演で使用するパワーポイントのデータ

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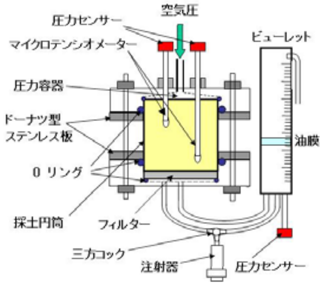
平成 20 年度 10 月 19 日（三重大学にて）

マルチステップ法による水分移動特性の推定

Estimation of soil hydraulic property using a multi-step method



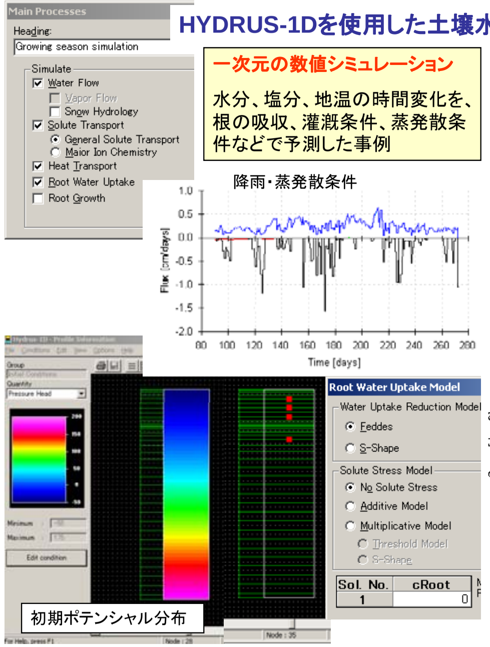
鳥取大学乾燥地研究センター

井上光弘

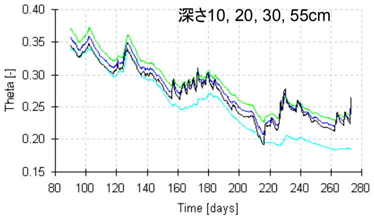
HYDRUS-1Dを使用した土壌水分と溶質濃度の経時変化の計算

一次元の数値シミュレーション

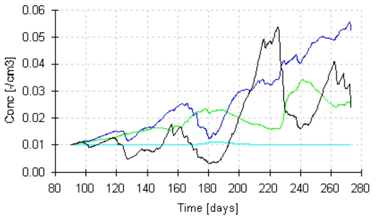
水分、塩分、地温の時間変化を、根の吸収、灌漑条件、蒸発散条件などで予測した事例



初期ポテンシャル分布



深さ別の土壌水分量の変化

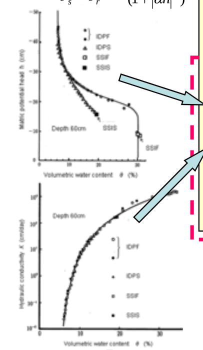


深さ別の溶質濃度の変化

数値シミュレーションに必要な土壌水分・溶液移動特性値の決定法

数値シミュレーションを行うには， 何が入力データとして必要で， 何が結果としてわかるのか？

$$S_e(h)=\frac{\theta(h)-\theta_r}{\theta_s-\theta_r}=\frac{1}{(1+|\alpha h|^n)^m}$$



$$K(h)=K_s S_e^{\ell}\left[1-\left(1-S_e^{1/m}\right)^m\right]^2$$

入力データとして

初期条件

境界条件

水分移動特性値
（水分保持曲線，
不飽和透水係数）

溶質移動特性値
（分散係数など）

数値シミュレーション

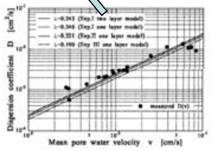
出力データ

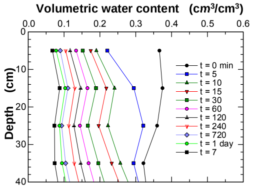
水分分布　θ(x, y, t)

圧力分布Ψ(x, y, t)

流速分布　q(x, y, t)

濃度分布C(x, y, t)





ある灌漑条件下の土壌中の水分・塩分プロフィルの時間変化を推定できる。

定常浸潤法による現場飽和透水係数

現場飽和透水係数を測定する方法として，プレッシャーインフィルトロメータを導入した。これは，定水頭で土壌中に侵入する水量を測定して，土壌の透水性を評価する方法である。

図 に示すように，半径aの円筒を土壌表面から深さdまで挿入し，マリオット給水装置を用いて水頭Hを一定に保つ。マリオット給水装置の有効断面積A [L^2]と単位時間に低下する水位R [LT^{-1}]を測定する。これらの値から，浸潤量Q_S [L^{3}T^{-1}] = $A\,R$と，定常浸潤フラックス$q_S = Q_S / (\pi a^2)$ を計算する。

ある定水頭$H1$の条件で，定常浸潤量$QS1$を測定して現場飽和透水係数K_{fS}を

$$K_{fS}=\frac{\alpha^* G Q_{S1}}{a\alpha^* H_1 + a + G\alpha^* \pi a^2} \quad \cdots\cdots\cdots (1)$$

の式で求める。ここで，$G = 0.316\ (d / a) + 0.184$である。

1個の設定水位で現場飽和透水係数を求めるためには，土壌パラメータα*が土壌ごとに別途，決められている。

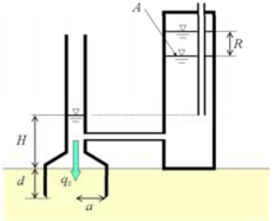


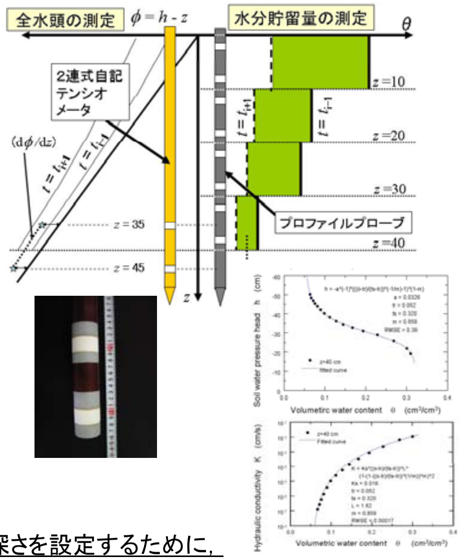
図　定水頭浸潤法の装置の概要

定常浸潤計の測定精度

森井俊広・井上光弘・竹下祐二:プレッシャーインフィルトロメータ法を用いた原位置透水試験の測定精度, 農業土木学会論文集　第207号, p.29-37 (2000)

内部排水法

二重円筒浸潤法の装置の中央に，**プロファイルプローブ**を挿入し，データロガー（現場用に電池で稼動する安価なものが好ましい）で電圧を測定して水分貯留量の時間変化を測定する。測定対象領域の底部に**2連式自記テンシオメータ**を設置し，同様にデータロガーで電圧を測定する。



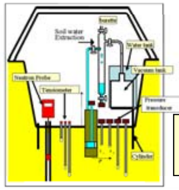
$$K = \frac{\left(\frac{\partial W_z}{\partial t}\right)_{z=Zn}}{\left(\frac{\partial \phi}{\partial z}\right)_{t=ti}}$$

正確な測定深さを設定するために，

2連式自記テンシオメータの開発

井上光弘・森井俊広・西村　拓・藤巻晴行：プロファイル水分計を用いた不飽和透水係数の原位置試験法，農業土木学会論文集　第231号，p.39-45 (2004)

多段吸引抽出法



実験

図21　多段吸引抽出法（屋外法）

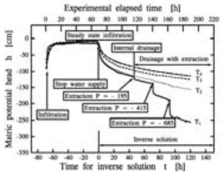


図22　多段吸引抽出法におけるポテンシャルの推移

$$OF(b) = W_q \sum_{i=1}^{N_1} \{w_i[q_m(t_i) - q_o(t_i, b)]\}^2 + W_h \sum_{i=1}^{N_2} \{v_i[h_{1m}(t_i) - h_{1o}(t_i, b)]\}^2$$

逆解析

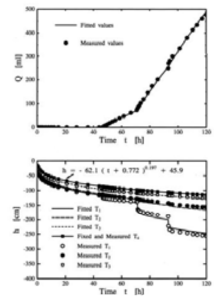


図23　多段吸引抽出法の抽出量とポテンシャルの推移，並びに予測との比較

水分移動特性値

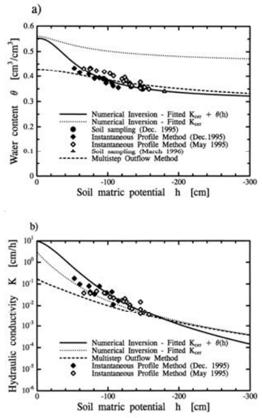


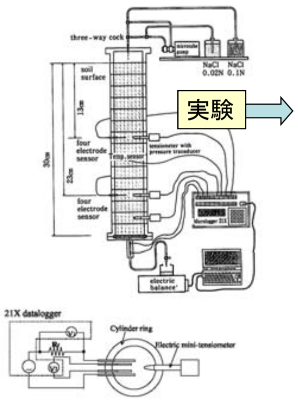
図24　多段吸引抽出法による土壌水分保持曲線，不飽和透水係数と水分量の関係

多段吸引抽出法の開発

精度の高い実験のための，工夫と，装置の開発が大切である。

Inoue, M., J.Simunek, J.W.Hopmans and V.Clausnitzer：In situ estimation of soil hydraulic functions using a multistep soil-water extraction technique, Water Resources Research, Vol.34, No.5, p.1035-1050 (1998)

水分・溶質移動特性値の同時逆解析法



実験

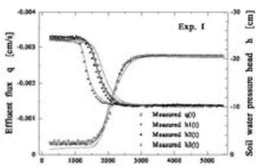


図26　非定常浸潤のフラックスと圧力水頭の推移，並びに予測との比較

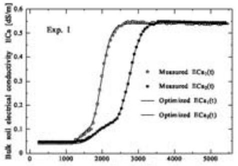


図27　非定常浸潤の塩分濃度の推移，並びに予測との比較

逆解析

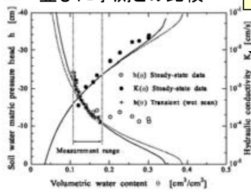


図28　同時逆解析法による水分移動特性値（水分特性曲線と不飽和透水係数）

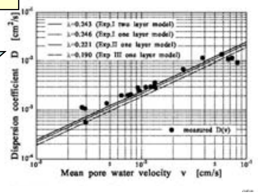


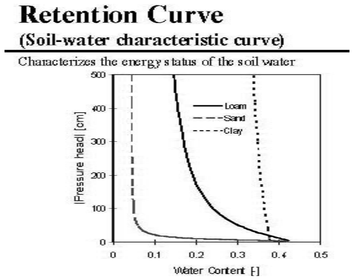
図29　同時逆解析法による溶質移動特性値（分散係数*D*，分散長λ，平均間隙流速*v*）

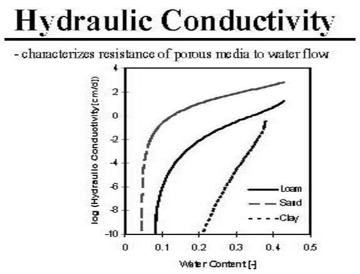
室内実験方法を圃場実験に拡張するために工夫が必要。

水分・溶質移動特性値の同時逆解析法の開発

Inoue, M., J.Simunek, S. Shiozawa, and J.W.Hopmans：Simultaneous estimation of soil hydraulic and solute transport parameters from transient infiltration experiments, Advances in Water Resources, Vol.23, p.677-688 (2000)

マルチステップ法は，不飽和土の保水性，透水性を定量的に把握することを目的とし，**水分保持曲線**と**不飽和透水係数**の関数式に含まれるパラメーターを逆解析手法で決定する方法である。





- ◆ **van Genuchten [1980]:**

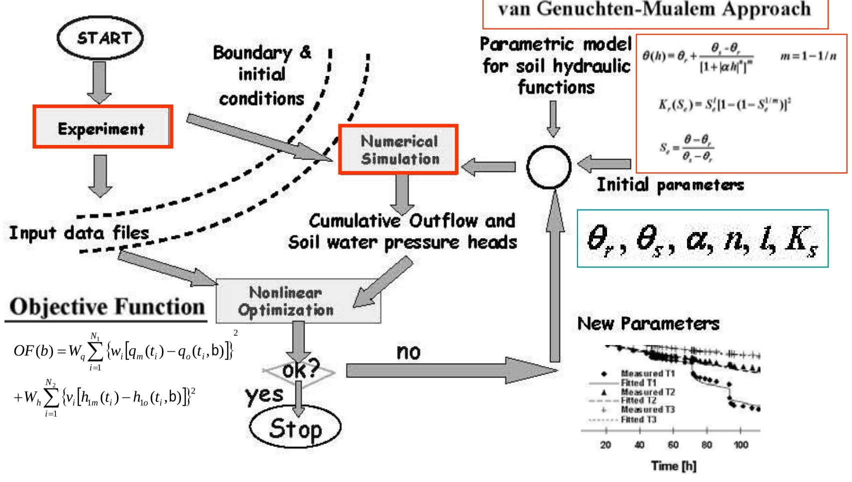
$$S_e = \frac{1}{(1+|\alpha h|^n)^{1-1/n}}$$

- ◆ **van Genuchten [1980]: (Mualem [1976])**

$$K(h) = K_s S_e^l \left[1 - \left(1 - S_e^{1/m}\right)^m\right]^2$$

逆解析の考え方

Analysis Structure and Flowchart



van Genuchten-Mualem Approach

START

Experiment

Boundary & initial conditions

Numerical Simulation

Parametric model for soil hydraulic functions

$$\theta(h)=\theta_r+\frac{\theta_s-\theta_r}{[1+|\alpha h|^n]^m} \qquad m=1-1/n$$

$$K_r(S_e)=S_e^l[1-(1-S_e^{1/m})]^2$$

$$S_e=\frac{\theta-\theta_r}{\theta_s-\theta_r}$$

Initial parameters

$$\theta_r,\ \theta_s,\ \alpha,\ n,\ l,\ K_s$$

Input data files

Cumulative Outflow and Soil water pressure heads

Nonlinear Optimization

ok?

yes

no

Stop

New Parameters

Objective Function

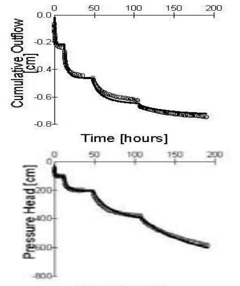
$$OF(b)=W_q\sum_{i=1}^{N_1}\{w_i[q_m(t_i)-q_o(t_i,\mathrm{b})]\}^2$$
$$+W_h\sum_{i=1}^{N_2}\{v_i[h_{1m}(t_i)-h_{1o}(t_i,\mathrm{b})]\}^2$$

Inverse Methods - Laboratory:

One- and Multi-step Methods:
Kool et al. (1985) and Parker et al. (1985) - onestep method
Russo (1988) - influence of parametric form
Toorman et al. (1992) - uniqueness problems
van Dam et al. (1992, 1994) - multistep method
Eching and Hopmans (1993, 1994) - one- and multi-step with *h*

Evaporation Method:
Feddes et al. (1988)
Ciollaro and Romano (1995)
Santini et al. (1995)
Šimunek et al. (1998)

Multi-Step Outflow Method



Inverse Methods - Field

Instantaneous Profile Method: Dane and Hruska (1983)

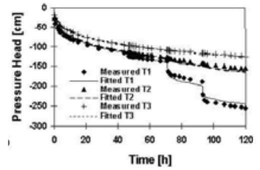
Ponded Infiltration:
Russo et al. (1991)
Bohne et al. (1992)

Tension Disc Infiltrometer:
Šimunek and van Genuchten (1996, 1997), Šimunek et al. (1998a,b)

Multistep Extraction Experiment: Inoue et al. (1998)

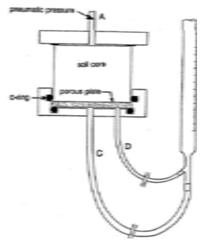
Cone Penetrometer:
Gribb (1996), Gribb et al. (1998), Kodesova et al. (1998)

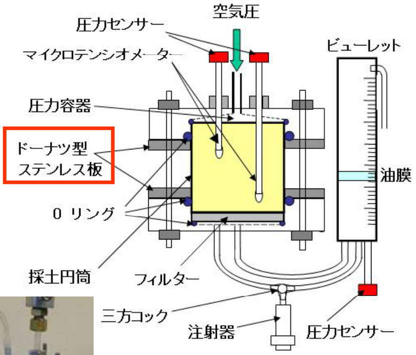
Multistep Extraction Experiment

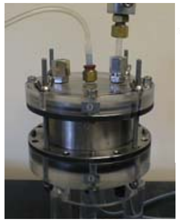


Inoue, M., J.Simunek, J.W.Hopmans and V.Clausnitzer: In situ estimation of soil hydraulic functions using a multistep soil-water extraction technique, Water Resources Research, Vol.34, No.5, p.1035-1050 (1998)

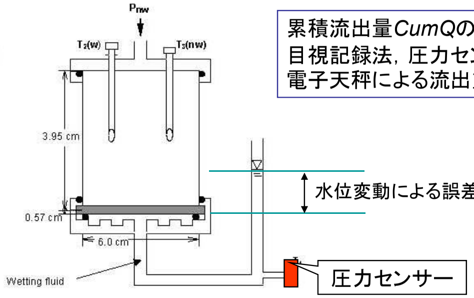
マルチステップ流出法の装置は，定常法，準定常法，非定常法に使用できる。**加圧条件下で空気が容器内から漏出しないように**，ドーナツ型ステンレス板を用いて，圧力容器の機密性が改良された（井上，1996，1997；森ら，2001）。



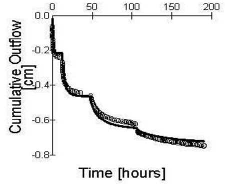


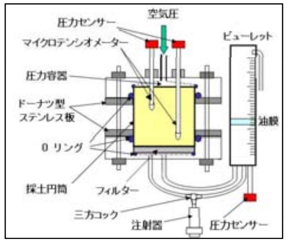


累積流出量*CumQ*の計測は，ビューレットによる目視記録法，圧力センサーによる水位自記法，電子天秤による流出重量自記法などがある。



圧力センサーによる水位自記法



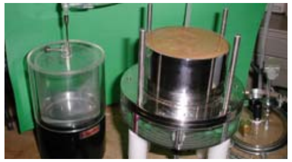


ビューレットによる目視記録法

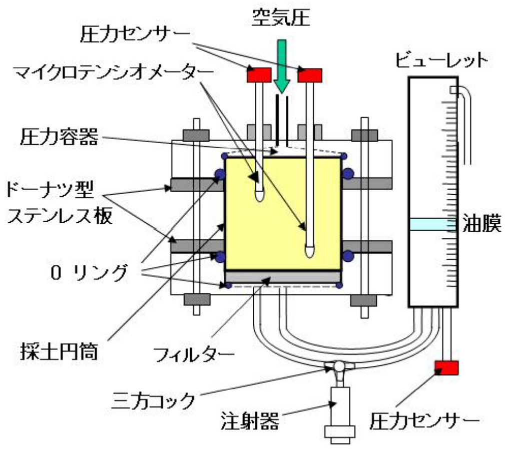
電子天秤による流出重量自記法

現場から定容積採土法等によって不撹乱状態で土壌を採取する。採土円筒は，内径50mm，高さ51mmの容積（V）100cm^{3}の容器，あるいは，内径84.6mm，高さ64mmの容積（V）360cm^{3}の容器など種々の大きさがあり，定容積採土法と同じ容器を使用する。フィルターには，100kPa用ハイフローセラミックフィルター（砂質土では焼結ガラスフィルター）を用い，試験の前後にフィルターの飽和透水係数を求める。


100kPa用ハイフロー
セラミックフィルター

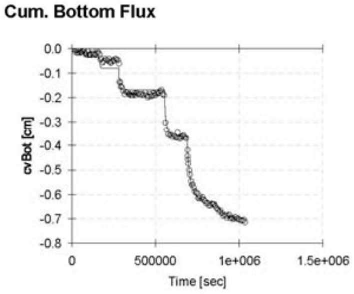

ビューレットに水を入れ下部試料
受器から供試体を飽和させる。

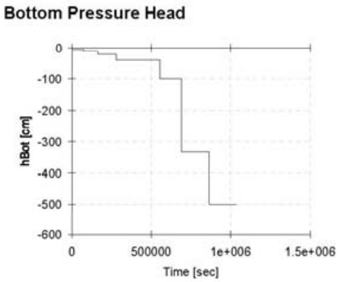
フィルター部下端の空間に気泡があれば，注射器と三方コックを用いて一方向の水流を発生させて気泡をビューレットに導く。ビューレットからオーバーフローした流出量あるいはマリオットタンクによる給水量，圧力容器の中に2本のテンシオメーターを異なる深さに挿入して供試体の動水勾配を測定し，定常浸潤法により土の飽和透水係数を求める。



自動圧力調節器を用いて，供試体上部から空気圧を段階的に加える。設定した空気圧に対して流出量がなくなり，ほぼ平衡状態とみなせる状態（準定常状態）に達したら，更に段階的に空気圧を加える。この準定常法では時間がかかるが，平衡に達する前に，次のステップに移行する非定常法を採用する。多くの土の場合，初期値を30cmH_2Oとして，段階的に60cmH_2O, 120cmH_2O, 240cmH_2O, 400cmH_2O, 600cmH_2O, 850cmH_2Oと約8時間ごとに空気圧を上昇させる。これらの値は砂質土の場合，初期値を10cmH_2Oとして，20cmH_2O, 30cmH_2O, 40cmH_2O, 50cmH_2O, 100cmH_2Oと空気圧を上昇させるなど，土の種類により異なる。

測定項目としては，空気圧，圧力水頭，累積流出量の経時変化を計測する。





測定終了後に供試体を取り出して炉乾燥法で実験終了時の体積含水率θfと乾燥密度を測定する。飽和体積含水率θ_sは，θ_fと測定したデータ累積流出量$CumQ$の経時変化から，$\theta_s = CumQ / V + \theta_f$で計算する。

準定常法による水分特性曲線は，設定した空気圧に対して測定した体積含水率θと圧力水頭h_pの関係から決定する。空気圧を一定に維持している段階の平衡状態の体積含水率θ□は，実験終了時の体積含水率θ_fと測定したデータ累積流出量$CumQ$の経時変化から，同一時間の測定値を用いて，$\theta(t) = CumQ(t) / V + \theta_f$で計算する。

一方，圧力水頭h_p (cm)は，

$$h_p = h_t - h_a \qquad (1)$$

で計算する。ここで，h_t：テンシオメーターで測定したポーラスカップの位置の圧力水頭(cm)，h_a：供試体に加圧された空気圧（水頭換算，cmH_2O）である。

マルチステップ流出法の実験データから，いろいろな組合せで目的関数を選択して，物性値のパラメーターを決定できる。

$$OF(b) = W_Q \sum_{i=1}^{N} \{w_i [CumQ_m(t_i) - CumQ_o(t_i, b)]\}^2 + W_h \sum_{i=1}^{M_1} \{v_i [h_{1m}(t_i) - h_{1o}(t_i, b)]\}^2$$

逆解析では，実験による圧力水頭（h_p）の経時変化と累積流出量(*CumQ*)の経時変化との残差が最小になるようにLevenberg－Marquardt法によって水分移動特性値のパラメーターを得る。ここで，残差としての目的関数*OF(b)*は，

$$\begin{aligned}OF(b) &= W_Q\sum_{i=1}^{N}\{w_i[CumQ_m(t_i)-CumQ_o(t_i,b)]\}^2\\ &+W_h\sum_{i=1}^{M_1}\{v_i[h_{1m}(t_i)-h_{1o}(t_i,b)]\}^2\\ &+W_h\sum_{i=1}^{M_2}\{v_i[h_{2m}(t_i)-h_{2o}(t_i,b)]\}^2 \qquad (8)\\ &+W_j\sum_{j=1}^{L}\{u_j[\theta_m(h_j)-\theta_o(h_j,b)]\}^2\\ &+W_g\sum_{g=1}^{G}\{y_g[k_m(h_g)-k_o(h_g,b)]\}^2\end{aligned}$$

で与えられ，*CumQ*, *h*, *θ*, *k* はそれぞれ，累積流出量，圧力水頭，体積含水率，不飽和透水係数で，*W*は無次元化係数，*v*, *u*, *y*は実験の重み係数，添え字mは実験値，添字oは数値実験値を意味する。

残差としての目的関数*OF(b)*は，いろいろな測定値を選択することが可能である。

① 累積流出量*CumQ*(*t*)のデータのみを用いる場合

② 試料の中心点で，圧力水頭$h_p(t)$ のデータのみを用いる場合

③ *CumQ*(*t*)と圧力水頭$h_p(t)$を用いる場合

④ 圧力水頭$h_{p1}(t)$と$h_{p2}(t)$を用いる場合

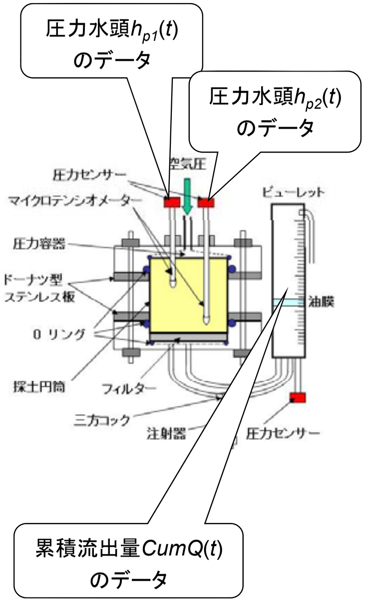
⑤ *CumQ*(*t*)と圧力水頭$h_{p1}(t)$と$h_{p2}(t)$を用いる場合

⑥ *CumQ*(*t*)と*hp*(*t*)に加えて，準定常法の水分特性曲線θ(h_p)のデータを含める場合

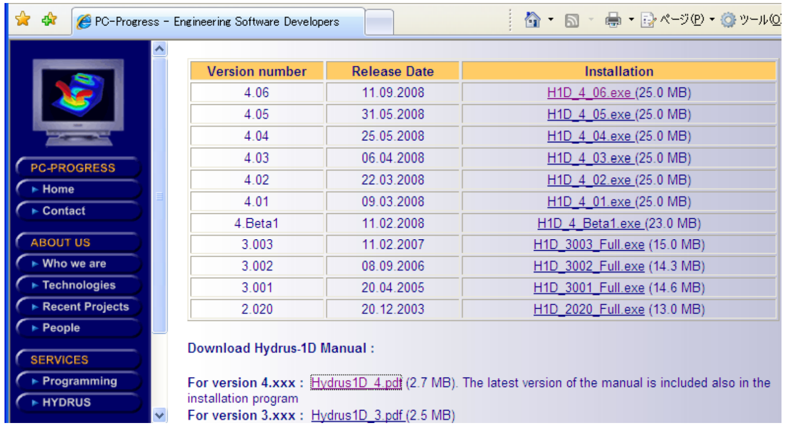
⑦ *CumQ* (*t*)と$h_p(t)$に加えて，別の水分特性曲線と不飽和透水係数*K*(h_p)のデータを含める場合

⑧ 上記の他に，種々のデータを組み合わせて逆解析が可能である。

基本的に，目的関数*OF(b)*には，累積流出量*CumQ*(*t*)を含める組み合わせが推奨されている。



使用するソフトウェアー　Hydrus-1D Version 4.06 (11 Sep. 2008)



Version number	Release Date	Installation
4.06	11.09.2008	H1D_4_06.exe (25.0 MB)
4.05	31.05.2008	H1D_4_05.exe (25.0 MB)
4.04	25.05.2008	H1D_4_04.exe (25.0 MB)
4.03	06.04.2008	H1D_4_03.exe (25.0 MB)
4.02	22.03.2008	H1D_4_02.exe (25.0 MB)
4.01	09.03.2008	H1D_4_01.exe (25.0 MB)
4.Beta1	11.02.2008	H1D_4_Beta1.exe (23.0 MB)
3.003	11.02.2007	H1D_3003_Full.exe (15.0 MB)
3.002	08.09.2006	H1D_3002_Full.exe (14.3 MB)
3.001	20.04.2005	H1D_3001_Full.exe (14.6 MB)
2.020	20.12.2003	H1D_2020_Full.exe (13.0 MB)

Download Hydrus-1D Manual :

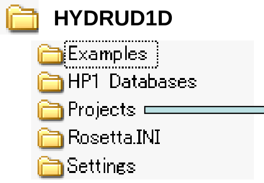
For version 4.xxx : Hydrus1D_4.pdf (2.7 MB). The latest version of the manual is included also in the installation program

For version 3.xxx : Hydrus1D_3.pdf (2.5 MB)

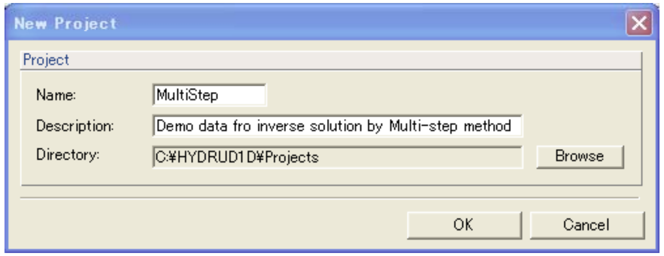
http://www.pc-progress.cz/Default.htm からダウンロードして，ソフトをインストールする.

使用するソフトウェアー　Hydrus-1D Version 4.06 (11 Sep. 2008)

プログラムをインストールする場合，自分で管理しやすいフォルダーにインストールする.



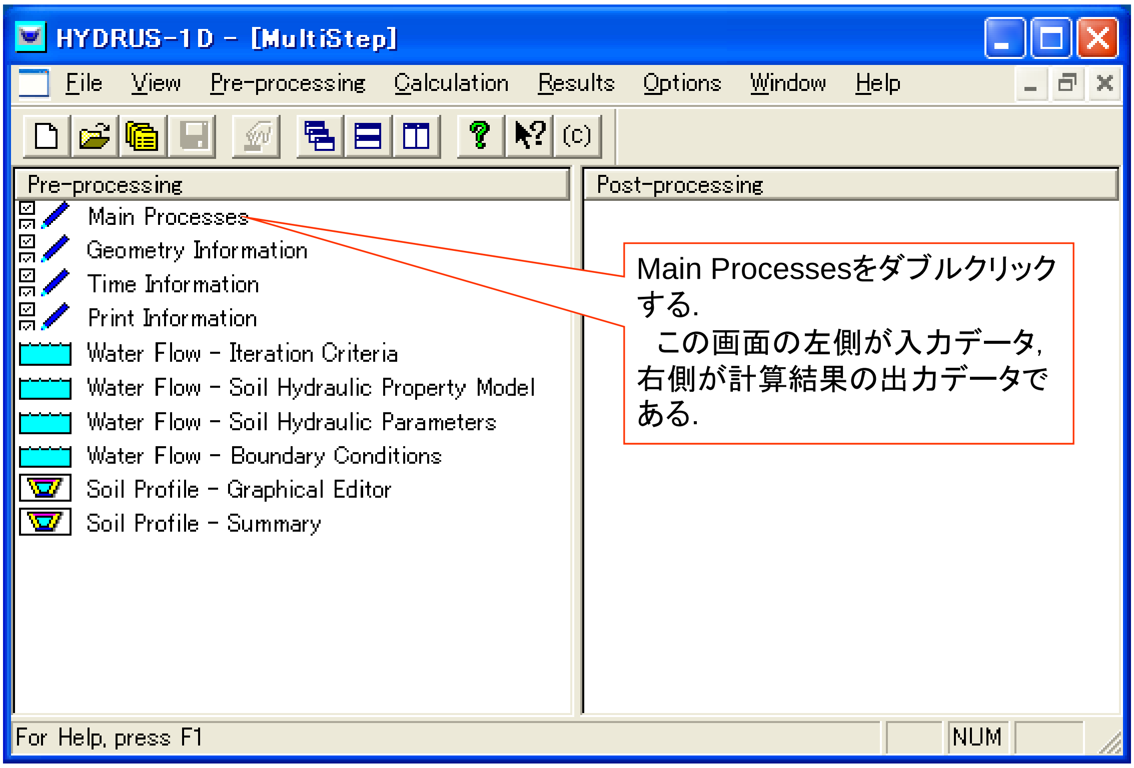
どのフォルダーに数値計算の入力値と出力値を管理するか理解することが重要である.



Name: MultiStep
Description: Demo data fro inverse solution by Multi-step method
Directory: C:¥HYDRUD1D¥Projects

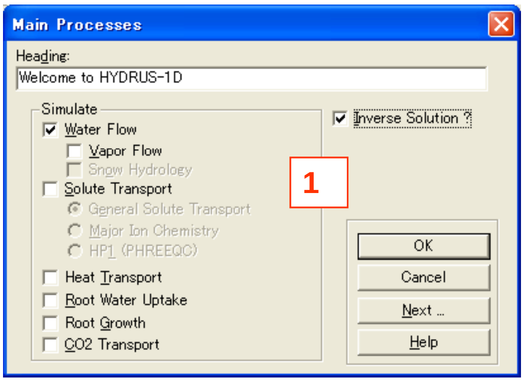
今回の演習では，C:¥HYDRUD1D/Projects の中に，MultiStepという名前で管理する.

使用するソフトウェアー　Hydrus-1D Version 4.06 (11 Sep. 2008)



Main Processesをダブルクリックする．
この画面の左側が入力データ，右側が計算結果の出力データである．

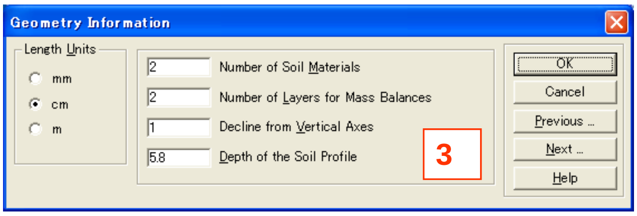
使用するソフトウェアー　Hydrus-1D Version 4.06 (11 Sep. 2008)



Heading:
Welcome to HYDRUS-1D

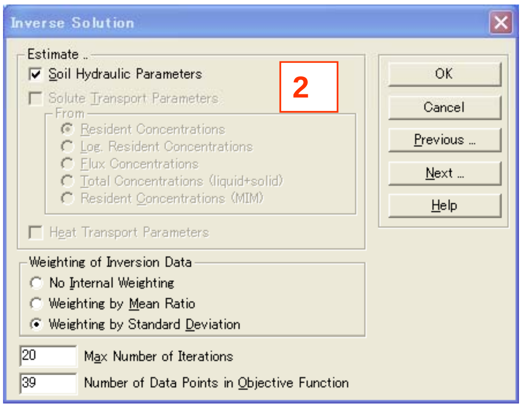
Simulate
☑ Water Flow
☐ Vapor Flow
☐ Snow Hydrology
☐ Solute Transport
● General Solute Transport
○ Major Ion Chemistry
○ HP1 (PHREEQC)
☐ Heat Transport
☐ Root Water Uptake
☐ Root Growth
☐ CO2 Transport

☑ Inverse Solution ?



Length Units
○ mm
● cm
○ m

2 Number of Soil Materials
2 Number of Layers for Mass Balances
1 Decline from Vertical Axes
5.8 Depth of the Soil Profile



Estimate
☑ Soil Hydraulic Parameters
☐ Solute Transport Parameters
From
● Resident Concentrations
○ Log. Resident Concentrations
○ Flux Concentrations
○ Total Concentrations (liquid+solid)
○ Resident Concentrations (MIM)
☐ Heat Transport Parameters

Weighting of Inversion Data
○ No Internal Weighting
○ Weighting by Mean Ratio
● Weighting by Standard Deviation

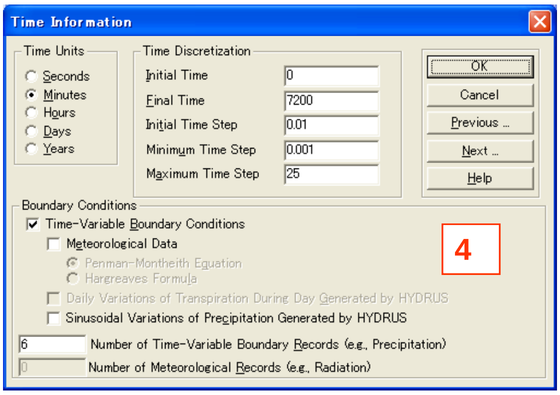
20 Max Number of Iterations
39 Number of Data Points in Objective Function

1 水分移動特性値を逆解析法で求めたいので，**Water Flow** と **Inverse Solution** にチェックを入れる．

2 Default のままで，変更はMax Number of Iterationsを1から20に，Number of Data Points in Objective Functionを1から39に変更する．

3 土壌層（5.1cm）とフィルター（0.7cm）の2層で実験を行ったので，1を2に変更し，Depth of the Soil Profileを100から5.8 (=5.1+0.7)に変更する．

使用するソフトウェアー　Hydrus-1D Version 4.06 (11 Sep. 2008)

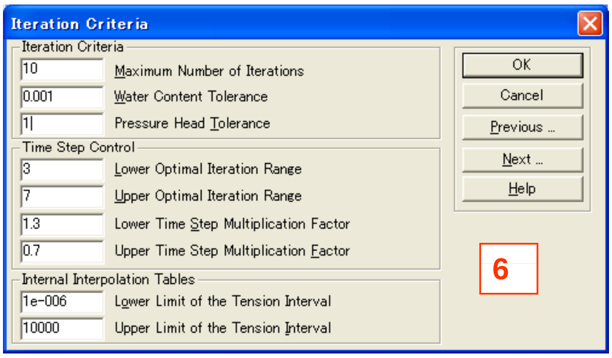


Time Information

Time Units
- ○ Seconds
- ● Minutes
- ○ Hours
- ○ Days
- ○ Years

Time Discretization
- Initial Time: 0
- Final Time: 7200
- Initial Time Step: 0.01
- Minimum Time Step: 0.001
- Maximum Time Step: 25

Boundary Conditions
- ☑ Time-Variable Boundary Conditions
- ☐ Meteorological Data
  - ● Penman-Montheith Equation
  - ○ Hargreaves Formula
- ☐ Daily Variations of Transpiration During Day Generated by HYDRUS
- ☐ Sinusoidal Variations of Precipitation Generated by HYDRUS
- 6 Number of Time-Variable Boundary Records (e.g., Precipitation)
- 0 Number of Meteorological Records (e.g., Radiation)

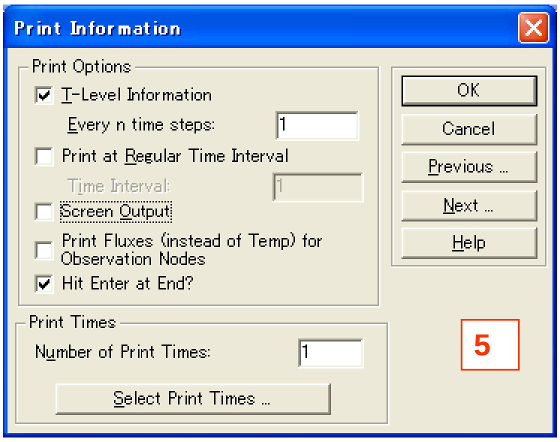


Iteration Criteria

Iteration Criteria
- 10 Maximum Number of Iterations
- 0.001 Water Content Tolerance
- 1 Pressure Head Tolerance

Time Step Control
- 3 Lower Optimal Iteration Range
- 7 Upper Optimal Iteration Range
- 1.3 Lower Time Step Multiplication Factor
- 0.7 Upper Time Step Multiplication Factor

Internal Interpolation Tables
- 1e-006 Lower Limit of the Tension Interval
- 10000 Upper Limit of the Tension Interval



Print Information

Print Options
- ☑ T-Level Information
  - Every n time steps: 1
- ☐ Print at Regular Time Interval
  - Time Interval: 1
- ☐ Screen Output
- ☐ Print Fluxes (instead of Temp) for Observation Nodes
- ☑ Hit Enter at End?

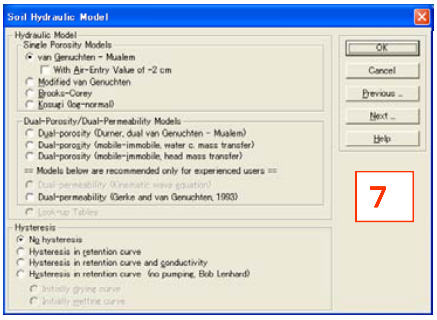
Print Times
- Number of Print Times: 1

4　Time UnitsをMinutesに，実験時間は5日で，圧力制御を6段階変化したので，Final Timeを7200とする．Meteorological Data のチェックを外す．

5　Default でScreen Outputのチェックを外す．

6　Default のままにする．

使用するソフトウェアー　Hydrus-1D Version 4.06 (11 Sep. 2008)



Soil Hydraulic Model

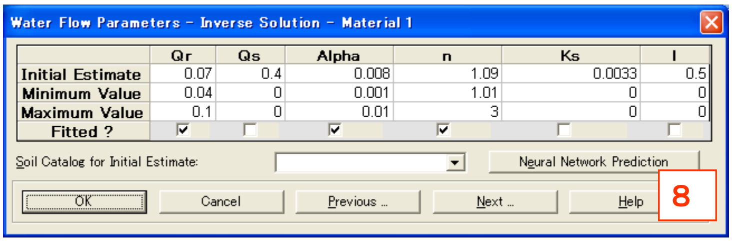
Hydraulic Model

Single Porosity Models
- ● van Genuchten - Mualem
  - ☐ With Air-Entry Value of -2 cm
- ○ Modified van Genuchten
- ○ Brooks-Corey
- ○ Kosugi (log-normal)

Dual-Porosity/Dual-Permeability Models
- ○ Dual-porosity (Durner, dual van Genuchten - Mualem)
- ○ Dual-porosity (mobile-immobile, water c. mass transfer)
- ○ Dual-porosity (mobile-immobile, head mass transfer)
- == Models below are recommended only for experienced users ==
- ○ Dual-permeability (Kinematic wave equation)
- ○ Dual-permeability (Gerke and van Genuchten, 1993)
- ○ Look-up Tables

Hysteresis
- ● No hysteresis
- ○ Hysteresis in retention curve
- ○ Hysteresis in retention curve and conductivity
- ○ Hysteresis in retention curve (no pumping, Bob Lenhard)
  - ○ Initially drying curve
  - ○ Initially wetting curve

7　Default のままで，水分移動特性値に van Genuchten – Mualem Modelを採用する．

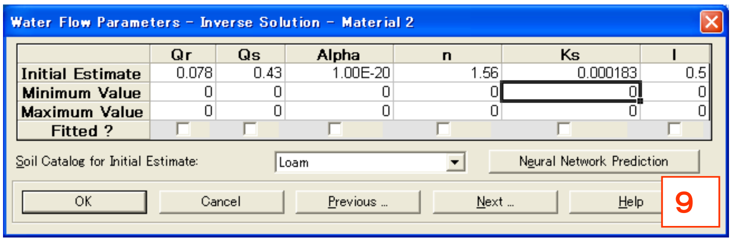


Water Flow Parameters - Inverse Solution - Material 1

	Qr	Qs	Alpha	n	Ks	l
Initial Estimate	0.07	0.4	0.008	1.09	0.0033	0.5
Minimum Value	0.04	0	0.001	1.01	0	0
Maximum Value	0.1	0	0.01	3	0	0
Fitted ?	☑	☐	☑	☑	☐	☐

Soil Catalog for Initial Estimate:

8　逆解析パラメータの初期値を入力する．実験で得られた値を尊重して，飽和水分量を0.4，飽和透水係数を0.0033 cm/min，係数ℓを0.5とする．残留水分量θr，係数α，nは任意の値を使用する．



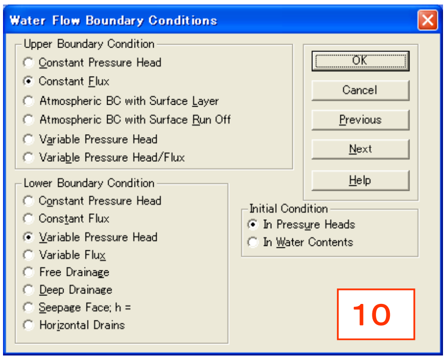
Water Flow Parameters - Inverse Solution - Material 2

	Qr	Qs	Alpha	n	Ks	l
Initial Estimate	0.078	0.43	1.00E-20	1.56	0.000183	0.5
Minimum Value	0	0	0	0	0	0
Maximum Value	0	0	0	0	0	0
Fitted ?	☐	☐	☐	☐	☐	☐

Soil Catalog for Initial Estimate: Loam

9　Material2 は，フィルターである．実験では空気侵入値が1バールのハイフローのセラミックフィルターを使用し，その飽和透水係数に0.000183cm/minを採用した．nの値，残留水分量と飽和水分量は何を使用しても問題ない．係数α は実験中空気が入らないので，小さな値として，1.00E-20を用いた．Fitted?は最適化するパラメータにチェックを入れる．

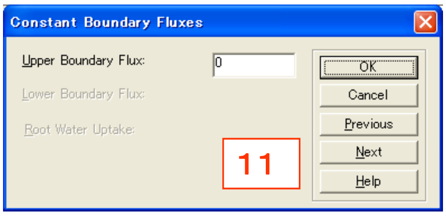
使用するソフトウェアー　Hydrus-1D Version 4.06 (11 Sep. 2008)



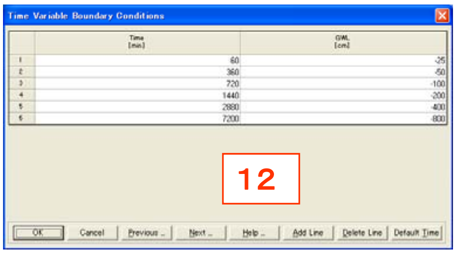
Upper Boundary Condition
○ Constant Pressure Head
● Constant Flux
○ Atmospheric BC with Surface Layer
○ Atmospheric BC with Surface Run Off
○ Variable Pressure Head
○ Variable Pressure Head/Flux

Lower Boundary Condition
○ Constant Pressure Head
○ Constant Flux
● Variable Pressure Head
○ Variable Flux
○ Free Drainage
○ Deep Drainage
○ Seepage Face; h =
○ Horizontal Drains

Initial Condition
● In Pressure Heads
○ In Water Contents



Upper Boundary Flux: 0
Lower Boundary Flux:
Root Water Uptake:

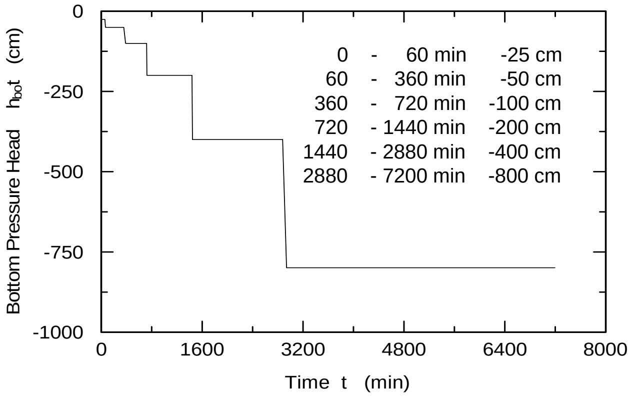


	Time [min]	GWL [cm]
1	60	-25
2	360	-50
3	720	-100
4	1440	-200
5	2880	-400
6	7200	-800

10　上部境界条件に，Constant Flux，下部境界条件に，Variable Pressure Head にチェックをいれて選択する．

11　上部境界では，フラックスは，蒸発もなく，灌漑などによる水の供給がないので，ゼロとする．

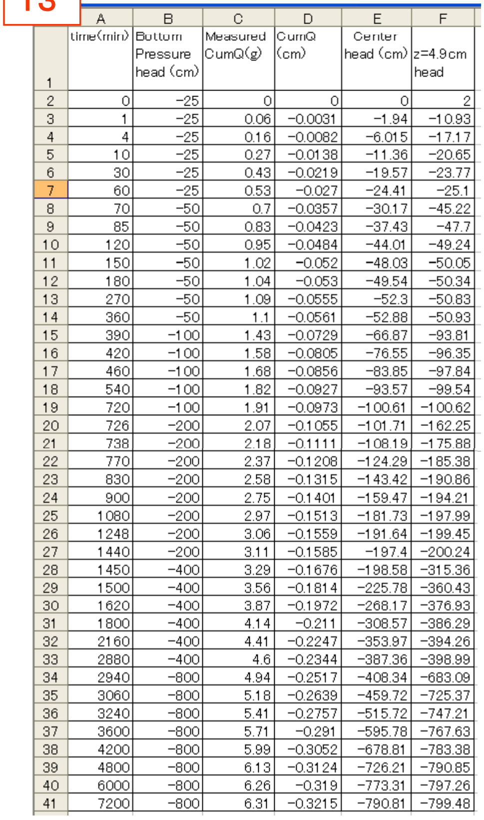
12　下部境界は，時間ゼロに瞬時に，-25cm の圧力を加え，その後，各時間ごとに，圧力を以下のように，変更した．



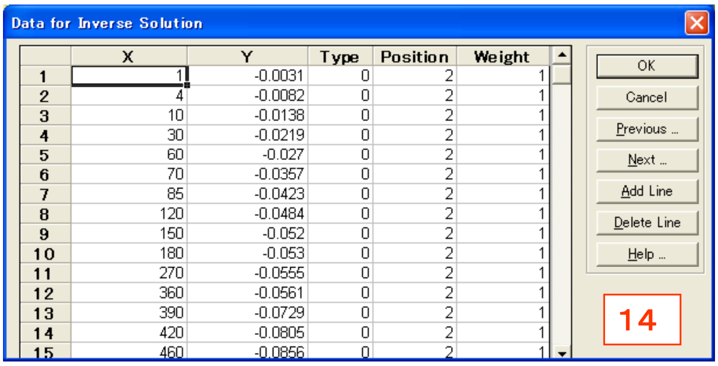
0	- 60 min	-25 cm
60	- 360 min	-50 cm
360	- 720 min	-100 cm
720	- 1440 min	-200 cm
1440	- 2880 min	-400 cm
2880	- 7200 min	-800 cm

使用するソフトウェアー　Hydrus-1D Version 4.06 (11 Sep. 2008)

13



1	time(min)	Bottom Pressure head (cm)	Measured CumQ(g)	CumQ (cm)	Center head (cm)	z=4.9cm head
2	0	−25	0	0	0	2
3	1	−25	0.06	−0.0031	−1.94	−10.93
4	4	−25	0.16	−0.0082	−6.015	−17.17
5	10	−25	0.27	−0.0138	−11.36	−20.65
6	30	−25	0.43	−0.0219	−19.57	−23.77
7	60	−25	0.53	−0.027	−24.41	−25.1
8	70	−50	0.7	−0.0357	−30.17	−45.22
9	85	−50	0.83	−0.0423	−37.43	−47.7
10	120	−50	0.95	−0.0484	−44.01	−49.24
11	150	−50	1.02	−0.052	−48.03	−50.05
12	180	−50	1.04	−0.053	−49.54	−50.34
13	270	−50	1.09	−0.0555	−52.3	−50.83
14	360	−50	1.1	−0.0561	−52.88	−50.93
15	390	−100	1.43	−0.0729	−66.87	−93.81
16	420	−100	1.58	−0.0805	−76.55	−96.35
17	460	−100	1.68	−0.0856	−83.85	−97.84
18	540	−100	1.82	−0.0927	−93.57	−99.54
19	720	−100	1.91	−0.0973	−100.61	−100.62
20	726	−200	2.07	−0.1055	−101.71	−162.25
21	738	−200	2.18	−0.1111	−108.19	−175.88
22	770	−200	2.37	−0.1208	−124.29	−185.38
23	830	−200	2.58	−0.1315	−143.42	−190.86
24	900	−200	2.75	−0.1401	−159.47	−194.21
25	1080	−200	2.97	−0.1513	−181.73	−197.99
26	1248	−200	3.06	−0.1559	−191.64	−199.45
27	1440	−200	3.11	−0.1585	−197.4	−200.24
28	1450	−400	3.29	−0.1676	−198.58	−315.36
29	1500	−400	3.56	−0.1814	−225.78	−360.43
30	1620	−400	3.87	−0.1972	−268.17	−376.93
31	1800	−400	4.14	−0.211	−308.57	−386.29
32	2160	−400	4.41	−0.2247	−353.97	−394.26
33	2880	−400	4.6	−0.2344	−387.36	−398.99
34	2940	−800	4.94	−0.2517	−408.34	−683.09
35	3060	−800	5.18	−0.2639	−459.72	−725.37
36	3240	−800	5.41	−0.2757	−515.72	−747.21
37	3600	−800	5.71	−0.291	−595.78	−767.63
38	4200	−800	5.99	−0.3052	−678.81	−783.38
39	4800	−800	6.13	−0.3124	−726.21	−790.85
40	6000	−800	6.26	−0.319	−773.31	−797.26
41	7200	−800	6.31	−0.3215	−790.81	−799.48



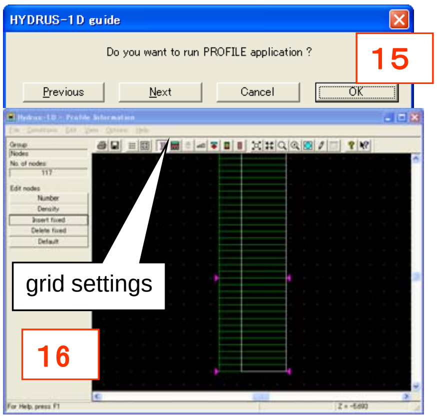
	X	Y	Type	Position	Weight
1	1	-0.0031	0	2	1
2	4	-0.0082	0	2	1
3	10	-0.0138	0	2	1
4	30	-0.0219	0	2	1
5	60	-0.027	0	2	1
6	70	-0.0357	0	2	1
7	85	-0.0423	0	2	1
8	120	-0.0484	0	2	1
9	150	-0.052	0	2	1
10	180	-0.053	0	2	1
11	270	-0.0555	0	2	1
12	360	-0.0561	0	2	1
13	390	-0.0729	0	2	1
14	420	-0.0805	0	2	1
15	460	-0.0856	0	2	1

13　マルチステップ法の実験データ．
テンシオメータをカラム中央と底部に挿入．
流出量は電子天秤で測定した．

14　逆解析に採用する累積流出量(cm)のデータを表から，ウィンドウのカット＆ペースト機能で貼り付ける．表中のX値が時間(min)で，Y値が累積流出量（上向きが正であるから，流出は下向きで負の値），Type, Position, Weightは，0, 2, 1である．

（必要であれば，headの値を入力する）

使用するソフトウェアー　Hydrus-1D Version 4.06 (11 Sep. 2008)


HYDRUS-1D guide

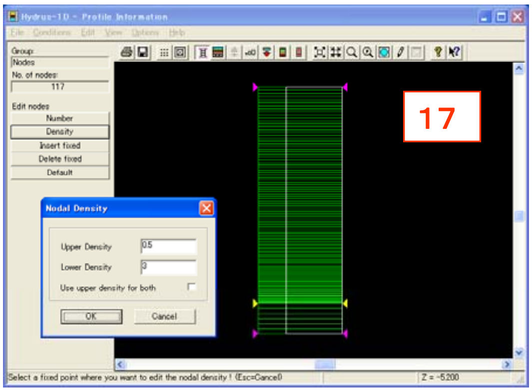
Do you want to run PROFILE application ?

For Help, press F1

15　OKを選択する.

16　計算領域の設定を行う.

カラムの高さは5.1cm, フィルターの厚さが0.7cmで, 土壌とフィルターを2層と考える. 土壌とフィルターの境界面を設定する. 5.8cmであるから, **Grid settings**で, No. of nodesを101から117に変更. spacingをWidth　Heightともに0.1に変更する. Insert fixedを5.1cmの場所に固定する.


Nodal Density

Upper Density: 0.5

Lower Density: 3

Use upper density for both ☐

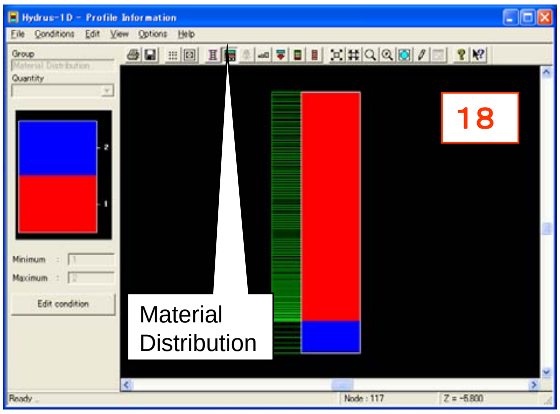
Select a fixed point where you want to edit the nodal density ! (Esc=Cancel)

Z = -5.200

17

Densityを上部を2, 下部を3にする. 5.1cmの場所で, upper Density を0.5　Lower Densityを3とする. これは, セラミックの上端で水分移動が著しく変化するので, その付近のノードの大きさを小さくし, 計算を安定させるためである.

使用するソフトウェアー　Hydrus-1D Version 4.06 (11 Sep. 2008)

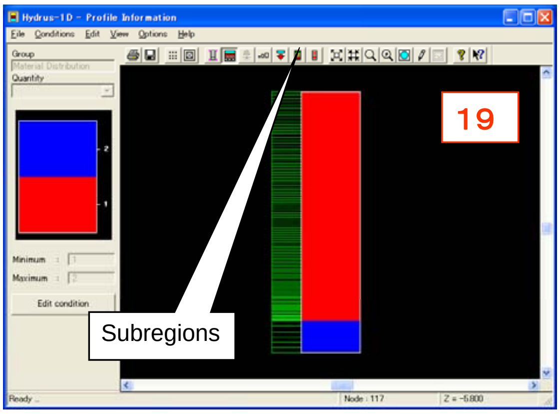


計算領域の設定を行う.

カラムの高さは5.1cm, フィルターの厚さが0.7cmで, 土壌とフィルターを2層と考える.

18

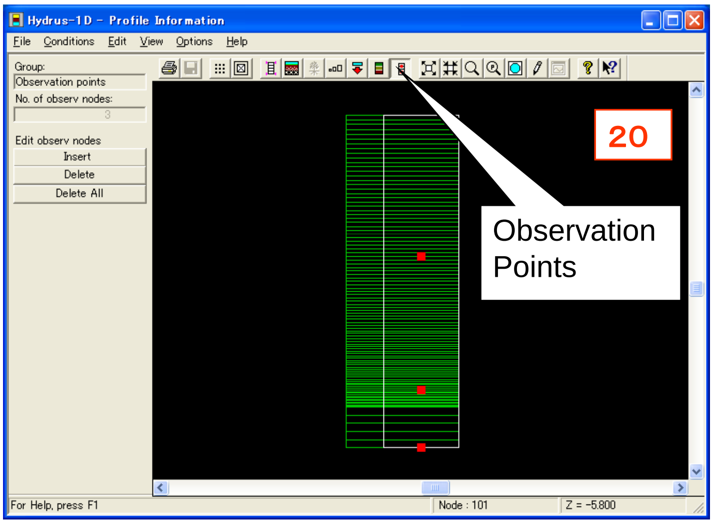
Material Distributionで, Edit conditionをクリックして, 手のマークが出たら, フィルターの部分をドラッグ, クリックして, Material index に2を入力してから, OKをクリックすると, 領域が赤から青に変化し, 2層に設定できたことが示される.



19

Subregionsで, Edit conditionをクリックして, 手のマークが出たら, フィルターの部分をドラッグ, クリックして, Subregion index に2を入力してから, OKをクリックすると, 領域が赤から青に変化し, 2層に設定できたことが示される.

使用するソフトウェアー Hydrus-1D Version 4.06 (11 Sep. 2008)


Hydrus-1D - Profile Information

Group: Observation points

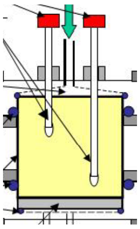
No. of observ nodes: 3

Node : 101

Z = -5.800

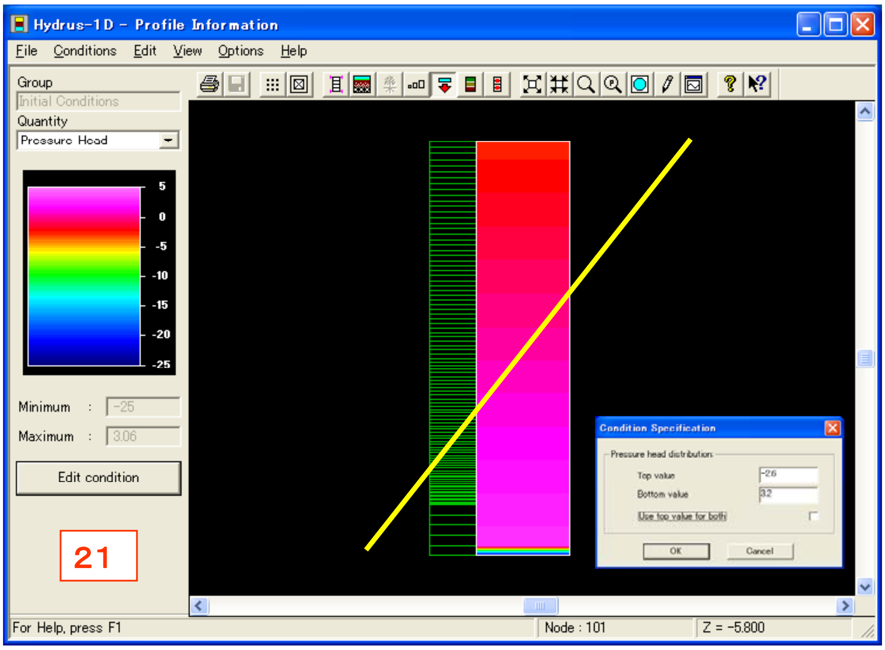
20 テンシオメータを挿入する場所を設定する.

Observation Pointsをクリックする．左側のEdit observ nodesのInsertをクリックして，手のマークが出たら，テンシオメータを挿入する，カラム中央とセラミックの上部2mmの部分でクリックすると，赤■のマークが表示され，Observation Pointsを設定したことが示される.



実験では，テンシオメータの設置位置を任意に決めることができる．マイクロテンシオメータを2点挿入することで，定常条件下でその水分状態の動水勾配から，ダルーシ則を用いて，不飽和透水係数を測定できる．また，テンシオメータで測定した圧力水頭から土壌のマトリックポテンシャルを計算して，その値を目的関数に採用できる.

使用するソフトウェアー Hydrus-1D Version 4.06 (11 Sep. 2008)


Hydrus-1D - Profile Information

Group: Initial Conditions

Quantity: Pressure Head

Minimum : -25

Maximum : 3.06

Condition Specification

Pressure head distribution

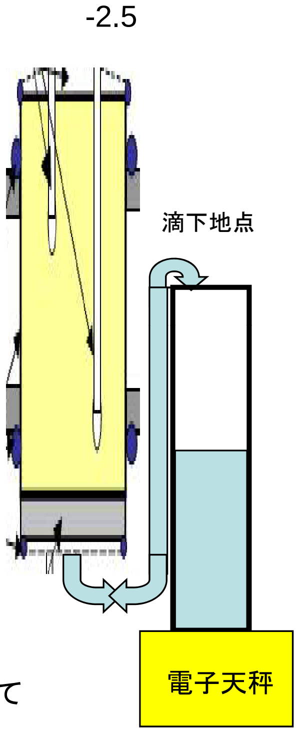
Top value: -2.6

Bottom value: 3.2

Use top value for both ☐

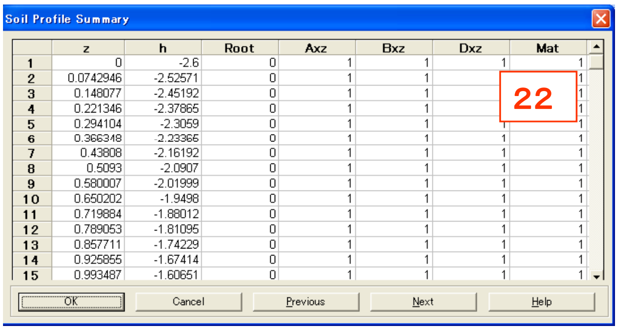
Node : 101

Z = -5.800



21 初期に流出口の滴下地点とフィルターの底部との高低差が2.5+0.7=3.2cmあり，初期の圧力分布は静水圧分布で安定しているが，時間ゼロでは，下部は空気圧によって，-25cmになる.

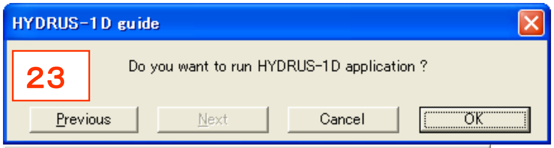
使用するソフトウェアー　Hydrus-1D Version 4.06 (11 Sep. 2008)



	z	h	Root	Axz	Bxz	Dxz	Mat
1	0	-2.6	0	1	1	1	1
2	0.0742946	-2.52571	0	1	1		1
3	0.148077	-2.45192	0	1	1		1
4	0.221346	-2.37865	0	1	1		1
5	0.294104	-2.3059	0	1	1	1	1
6	0.366348	-2.23366	0	1	1	1	1
7	0.43808	-2.16192	0	1	1	1	1
8	0.5093	-2.0907	0	1	1	1	1
9	0.580007	-2.01999	0	1	1	1	1
10	0.650202	-1.9498	0	1	1	1	1
11	0.719884	-1.88012	0	1	1	1	1
12	0.789053	-1.81095	0	1	1	1	1
13	0.857711	-1.74229	0	1	1	1	1
14	0.925855	-1.67414	0	1	1	1	1
15	0.993487	-1.60651	0	1	1	1	1

22

以上述べたように，計算領域の設定，計算に必要な初期ポテンシャル分布の設定，成層条件，テンシオメータ埋設位置などの観測点の情報を入力し終えて，データをセーブすると，初期ポテンシャル分布のデータが入力できたことが示される．

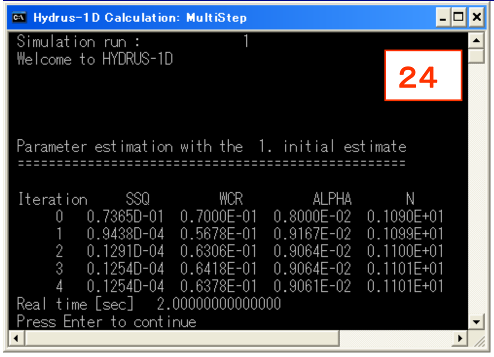


Do you want to run HYDRUS-1D application ?

23

逆解析を計算しても良いか？

OKをクリックする．



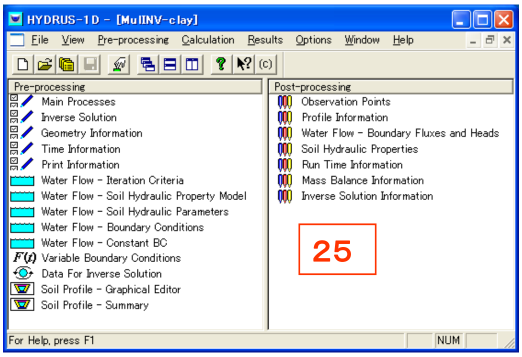
```
Simulation run :              1
Welcome to HYDRUS-1D



Parameter estimation with the  1. initial estimate
==================================================


Iteration     SSQ         WCR         ALPHA         N
      0   0.7365D-01  0.7000E-01  0.8000E-02  0.1090E+01
      1   0.9438D-04  0.5678E-01  0.9167E-02  0.1099E+01
      2   0.1291D-04  0.6306E-01  0.9064E-02  0.1100E+01
      3   0.1254D-04  0.6418E-01  0.9064E-02  0.1101E+01
      4   0.1254D-04  0.6378E-01  0.9061E-02  0.1101E+01
Real time [sec]   2.00000000000000
Press Enter to continue
```

24

計算の結果は，スクリーンに表示される．

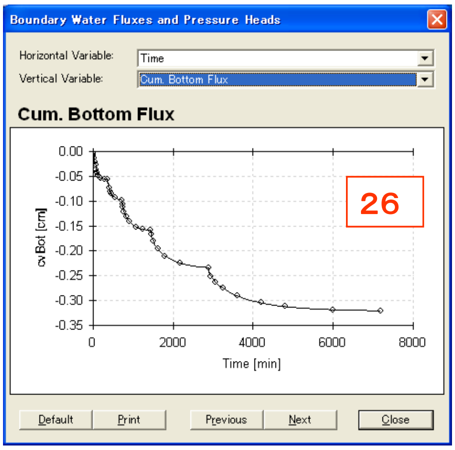
ここで，大切なことは，実験条件と同一の境界条件，初期条件を入力すること，また，初期パラメータの係数α，係数nの設定が重要である．一つは，土壌の土性や，シルト，粘土，砂の含有割合が参考になる．

使用するソフトウェアー　Hydrus-1D Version 4.06 (11 Sep. 2008)



25

計算が終了し，enterキーを押すと，右側のPost-processingに，計算結果が表示される．そこで，Water Flow-Boundary Fluxes and Headsをダブルクリックし，TimeとCum. Bottom Fluxの関係を表示させる．

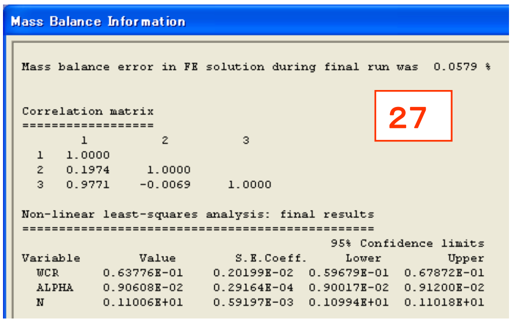


Horizontal Variable: Time

Vertical Variable: Cum. Bottom Flux

26

縦軸は単位面積を通過する累積流出量(cm)，横軸は時間(min)で，実験値と推定値が良く一致していることが示される．



```
Mass balance error in FE solution during final run was  0.0579 %


Correlation matrix
==================
        1          2          3
  1   1.0000
  2   0.1974     1.0000
  3   0.9771    -0.0069     1.0000

Non-linear least-squares analysis: final results
================================================
                                        95% Confidence limits
Variable        Value        S.E.Coeff.     Lower           Upper
  WCR       0.63776E-01    0.20199E-02  0.59679E-01  0.67872E-01
  ALPHA     0.90608E-02    0.29164E-04  0.90017E-02  0.91200E-02
  N         0.11006E+01    0.59197E-03  0.10994E+01  0.11018E+01
```

27

最終的に，逆解析によって得られたパラメータの信頼性の評価も表示される．

3.1 試験

試験を行う上の留意点として，

① 定常浸潤法で，それぞれの含水量に対して物性値を求める定常法と比べると，実験時間が少ない（長くても，約10日間で実験終了）。

② 装置自体は，比較的簡単な構成からなり，取り扱いが容易であり，不撹乱の土壌に対して実験できる。

③ 下部フィルターの透水係数を知る必要がある。

④ テンシオメーターのデータを用いる場合，圧力水頭が-850cm程度で，測定限界になる。

⑤ 例えば，テンシオメーターを使用しないで，300kPa用のフィルターを用いる場合には，累積流出量(*CumQ*)の経時変化のデータを基に，300kPaまでの特性値を決定できる。

⑥ 吸引法などの負圧実験と比べて，負圧状態での気泡の発生がないので，実験が容易である。

⑦ 土中に大きな礫を含むもの，乾燥に伴って著しく収縮する土には適用しにくい。

3.2 逆解析

マルチステップ流出法は，多くの土に対し適用され，市販のフリーソフトHYRDUS-1D(Simunekら，2005)や，フリーソフトWASH-1D（藤巻ら，2001）でパラメーターを推定できるがソフトの使用法を熟知する必要がある。

逆解析を行う上の留意点として，

① 試験を行った実験状況と同じ，初期条件，境界条件を与える必要がある。

② 下端フィルターの特性値の与え方に注意を要する。

③ 逆解析では，プログラムを実行して，巨視的な最小値を得るために，適当なパラメーターの初期値を決定する基礎知識が必要である。

④ ひとつの方法として，Echingら(1993)は，異なる初期値を与えて，いずれも同じ最適パラメーターになることを確認するアルゴリズムを採用しているので，参考になる。

⑤ 累積流出量(*CumQ*)の経時変化のみをデータとして使用する場合，パラメーターの初期値は極めて重要になる。1点でも，水分特性曲線θ(*hp*)のデータがあると逆解析が容易になる。

⑥ 入力データの累積流出量*CumQ*(*t*)，圧力水頭*hp*1(*t*)と*hp*2(*t*)などの時間変化のデータがばらつく場合は，逆解析は困難となる。

⑦ 信頼できる実験データに対して，重みをつけて逆解析することを奨励する。

3.3 まとめ

不飽和土の水分移動を定量的に把握するために，水分移動式として式(5)を採用していることが前提条件で，パラメーターの決定のために，van Genuchten式と Mualem式の代わりに，修正van Genuchten式，小杉の式，Brooks-Corey式，動水-不動水モデル式などを採用できる。実験の下端条件に圧力水頭の経時変化を境界条件に組み入れることができる。さらに，実験に合致した条件で逆解析を行うことが可能で，目的関数の中に，他の定常法で得られた物性値を加味できる特徴を有し，今後，普及する方法である。しかし，実験結果に依存するので，試験に対する経験と，逆解析を行うためのノウハウが必要で，少なくとも，論文に書かれていない苦労話は貴重な情報となる。

$$\frac{\partial \theta}{\partial t} = \frac{d\theta}{dh_p}\frac{\partial h_p}{\partial t} = \frac{\partial}{\partial z}\left[K(h_p)\frac{\partial h_p}{\partial z} + K(h_p)\right] \qquad \text{式(5)}$$

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森　也寸志・木原康孝・井上光弘・福島晟：マルチステップ流出法による不攪乱土壌の不飽和透水係数の推定，農業土木学会論文集，213，pp.61～68，(2001).

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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　朝田　景

はじめに

負圧浸入計(Perroux & White, 1988)
　飽和近傍の土壌の透水性を原位置で測定する装置
　（以下、原位置飽和透水係数：K_{wfs}）

長所
　土壌へのかく乱が最小限ですむ.
　水浸入へのマクロポアの寄与がわかる.

農学分野への適用

図1　負圧浸入試験の様子

負圧浸入計のデータを用いた逆解析による水分移動特性の推定

目的関数に浸入試験前後のディスク直下の
体積含水率を追加 (Simunek & van Genuchten, 1996, 1997)
→水分特性曲線が実測値と適合しない(Simunek et al., 1998).

目的関数に水分特性曲線のデータを追加
(Schwartz & Evett, 2002)
→手間がかかる.

浸入試験時の圧力水頭と土壌水分量を目的関数に加えること
によって，水分移動特性の推定値の精度が向上するか.

研究の目的

- 負圧浸入計を用いて，表層土における飽和近傍（0～－20cmH_2O程度）の原位置透水係数の決定
- より広い圧力水頭領域の水分移動特性を推定するための土壌水分量や圧力水頭の時間変化を用いた逆解析の検討

実験方法

調査圃場

- 東京農工大学FSセンター（東京都府中市）
  1993年～化学肥料と牛フンおがくず堆肥の連用
  小麦、トウモロコシ、小麦、大豆のローテーション

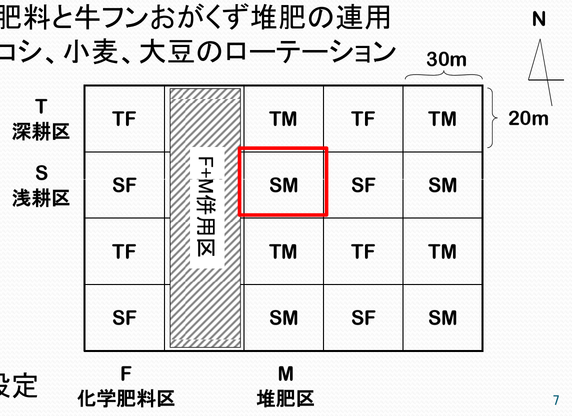


図2　試験区の設定

浸入試験

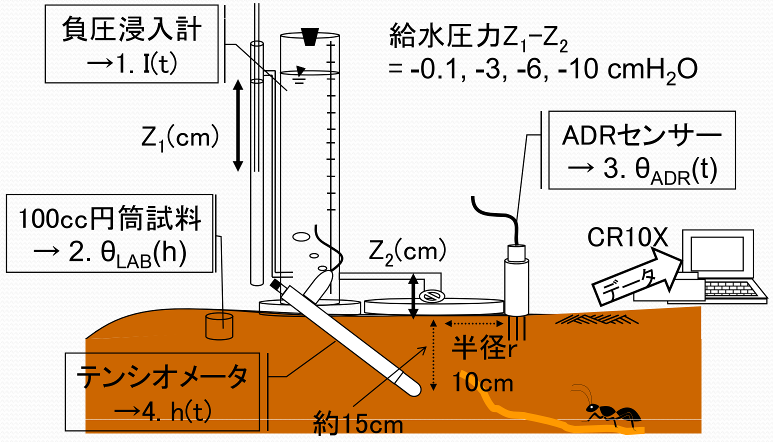


図3　浸入試験の様子

- 3. $\theta_{ADR}(t)$: ADRセンサー出力値, 比誘電率(V_w)と体積含水率(θ)の関係から(Sandy et al., 2005)推定

$$\theta = 0.001 + 1.531V_w + 2.342V_w^2 + 1.448V_w^3 \quad \cdots(1)$$

- 4. h(t):テンシオメータの出力電圧値(V_p)と圧力水頭(h)の関係から推定

$$h = (128.81 \times V_p + 114.79) - 15.0 \quad \cdots(2)$$

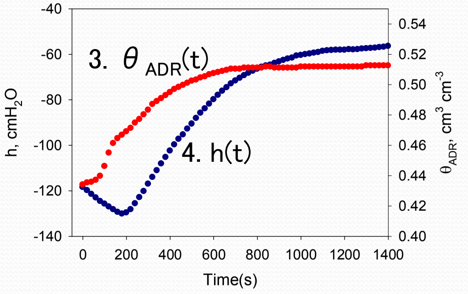


図4 浸入試験時の圧力水頭と土壌水分量の時間変化

土壌

黒ボク土(砂:0.32, シルト:0.32, 粘土:0.36)

乾燥密度:0.68Mg m^{-3}

土粒子密度*:2.72g cm^{-3}

間隙率:0.75

飽和透水係数:

5.76×10^{-3}cm s^{-1}

VGモデルパラメータの推定値(RETC):

Θr=0.391, Θs=0.699,

α=0.050, n=2.135

(*Sandy et al., 2005)

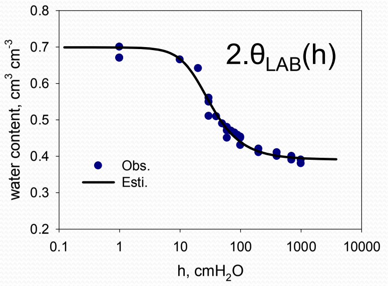
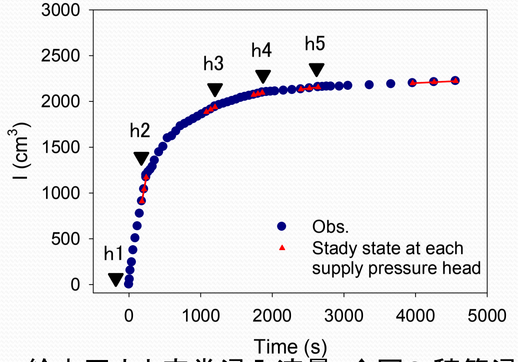


図5 水分特性曲線

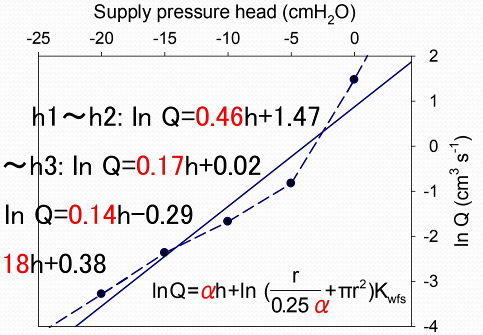
K_{wfs},K(h)の算出方法(例)(Reynols & Elrick, 1991)



↓表1 給水圧力と定常浸入流量, ↑図6 積算浸入量

cmH_2O	h1=-0.1	h2=-5	h3=-10	h4=-15	h5=-20
Q	4.36	0.44	0.19	0.09	0.04
ln Q	1.47	-0.83	-1.68	-2.37	-3.29

つづき



h1～h2: ln Q=0.46h+1.47

h2～h3: ln Q=0.17h+0.02

h3～h4: ln Q=0.14h−0.29

h4～h5: ln Q=0.18h+0.38

$$\ln Q = \alpha h + \ln\left(\frac{r}{0.25\,\alpha} + \pi r^2\right)K_{wfs}$$

↓表2 原位置透水係数, ↑図7 給水圧力と定常浸入流量

K(h)=K_{wfs}×exp(αh)	h1=-0.1	h2=-5	h3=-10	h4=-15	h5=-20
K_{wfs} (×10^{-3} cm s^{-1})	10.88	10.88	10.88	10.88	10.88
K(h) (×10^{-3}cm s^{-1})	**10.39**	**3.44**	**3.05**	**1.92**	**0.44**

逆解析の設定条件(HYDRUS−1D)

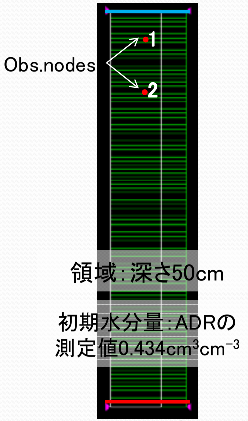


図8　一次元流れに
おける領域と境界条件

<u>初期条件</u>

θ_r, α, n, θ_s：推定値(RETC)

I: 0.5, K_s: K_{wfs}　K_s以外を推定

<u>境界条件</u>

上端: 変動圧力境界(Variable Pressure Head)

:−0.1, −3, −6, −10cmH_2O

下端: 自由排水境界(Free Drainage)

<u>目的関数</u>Φ

Φ［I(t)］

逆解析の設定条件(HYDRUS−2D)

（C¥hydrus2D3D¥Projects¥2D_Tests¥Disc）

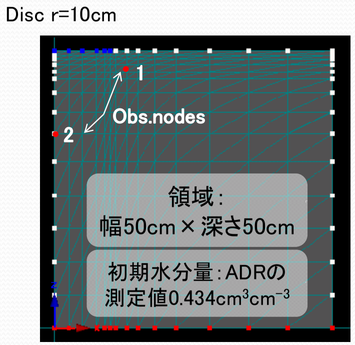


図9　軸対象モデルに
おける領域と境界条件

<u>初期条件</u>

θ_r, α, n, θ_s：推定値(RETC)

I: 0.5, K_s: K_{wfs}　K_s以外を推定

<u>境界条件</u>

上端: 変動圧力境界

−0.1, −3, −6, −10cmH_2O

下端: 自由排水境界

<u>目的関数</u>Φ

Φ［I(t), θ_{LAB}(h)］, Φ［I(t), θ_{ADR}(t)］

Φ［I(t), h(t)］, Φ［I(t), θ_{ADR}(t), h(t)］

HYDRUS−1D,−2Dの比較

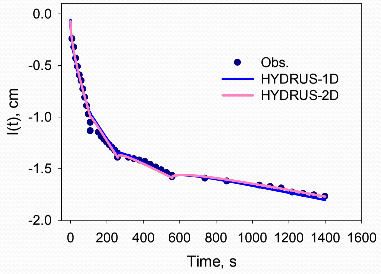


図10　積算浸入量*

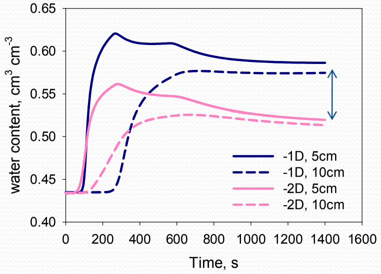


図11　ディスク下の土壌水分量*

*目的関数をI(t)のみとした場合

結果と考察

原位置飽和・不飽和透水係数K_{wfs},K(h)

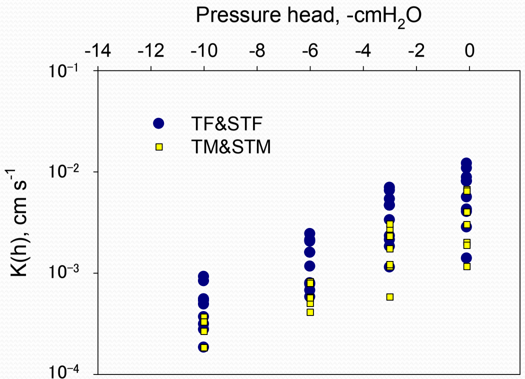


図１２　原位置透水係数 ［各試験区内の異なる地点で5～6回測定］

積算浸入量 I(t)　実測値と推定値の比較

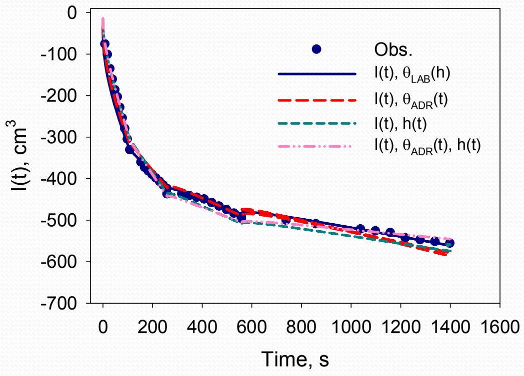


図１３ 積算浸入量

土壌水分量の時間変化 θ_{ADR}(t)

実測値と推定値の比較

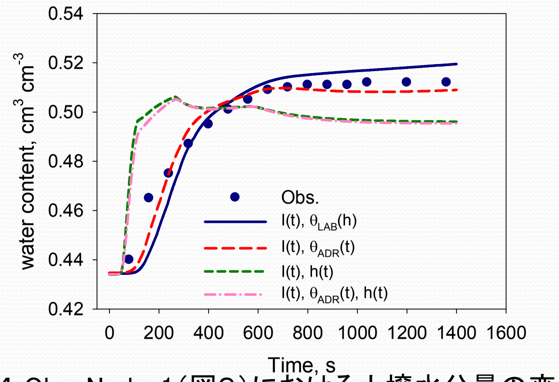


図１４ Obs. Nodes1（図９）における土壌水分量の変化

圧力水頭の時間変化 h(t)

実測値と推定値の比較

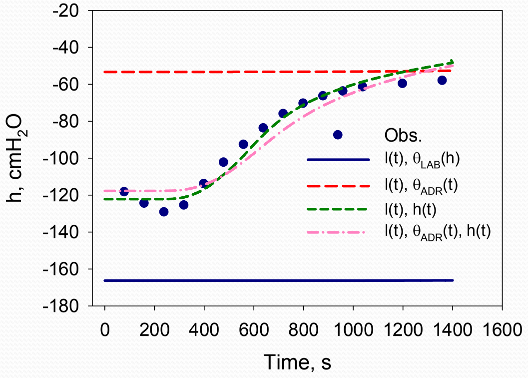


図15 Obs. nodes2（図9）における圧力水頭の変化

水分特性曲線 $\theta_{LAB}(h)$ 実測値と推定値の比較

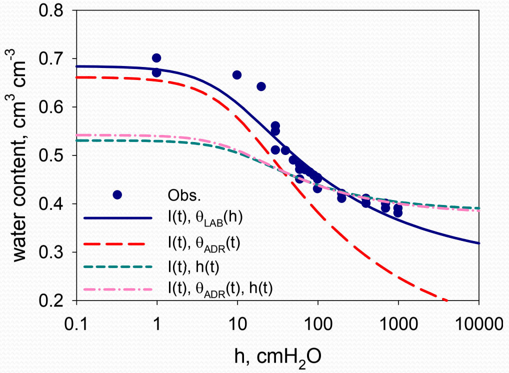


図16　水分特性曲線

不飽和透水係数　実測値と推定値の比較

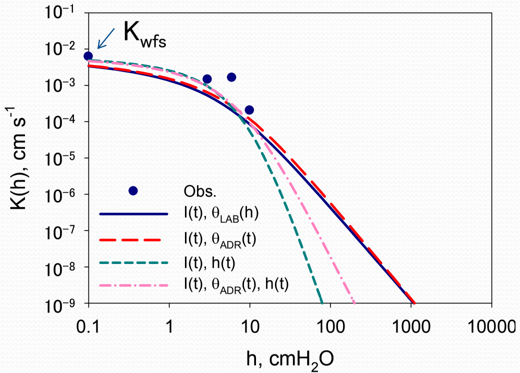


図17　不飽和透水係数

まとめ

負圧浸入計による飽和近傍の原位置透水係数と圧力水頭，土壌水分量の時間変化を用いて，より広い圧力水頭領域の水分移動特性を推定した．

- 土壌水分量，圧力水頭の時間変化を目的関数にすると，それぞれ，飽和近傍および低圧力領域の水分特性曲線を比較的よく説明できた．
- 不飽和透水係数の推定では，土壌水分量よりも圧力水頭を目的関数としたほうがK_{wfs}に近づいた．

部会の歴史

1．1987年　第26回　（昭和62年10月13,14日：岐阜）
土壌物理における新しい手法とその展開

2.　1988年，第27回　（昭和63年10月17日：京大会館）
粘土・水系の分散凝集と流動特性

3.　1989年，第28回　（昭和64年、平成元年9月27日：共済会館びわこ）
土壌・植物中の物質移動

4.　1990年，第29回　（平成2年11月19,20日）
水田土壌および湿地土壌の特徴
若手研究者からの話題

5.　1991年，第30回　（平成3年12月4日：福岡リーセントホテル）
海外における最近の土壌物理研究

6.　1992年，第31回　（平成4年
世界の水田の現状と発展方向

7.　1993年，第32回　（平成5年11月26日：茨城大学）
タイトルなし

8.　1994年，第33回　（平成6年
関連分野からみた土壌物理的諸問題

9.　1995年，第34回　（平成7年
土壌物理の新しい波

10　1996年，第35回　（平成8年
土壌物理に何を求めるか
―　環境保全型農業あるいは持続型農業を視野に入れて　―

11.　1997年，第36回　（平成9年
土中生物，土壌化学性と土壌の物理性

12.　1998年，第37回　（平成10年
土壌物理と水文学

13.　1999年，第38回　（平成11年
土壌の温度環境をめぐる諸問題

14.　2000年，第39回　（平成12年
乾燥地の土壌劣化をめぐる諸問題

15.　2001年，第40回　（平成13年12月5日：鳥取大学乾燥地研究センター）
乾燥地の土壌劣化をめぐる諸問題
―　フィールドワークを中心にして　―

16.　2002年，第41回　（平成14年
間隙レベルの土壌物理現象
―新たな展開に向けて―

17.　2003年，第42回　（平成15年
マクロレベルの土壌物理現象

18.　2005年，第43回　（平成16年1月8日：東京大学）
新しい人の土壌物理

19.　2005年，第44回　(平成17年10月14日：北海道大学)
環境の修復・保全と土壌物理

20.　2006年，第45回　(平成１８年10月15日：北海道大学)
期待される土壌物理学

21.　2007年，第46回　（平成19年10月14日：九州大学）
不飽和土中の水分・溶質移動モデルの研究と普及

農業農村工学会（旧農業土木学会）土壌物理研究部会規約

（名称）
第１条　この部会は，農業農村工学会（旧農業土木学会）土壌物理研究部会と称する。

（目的）
第２条　この部会は，土壌物理学に関する学術研究の発展及び部会員間の学術交流に寄与することを目的とする。

（事業）
第３条　この部会は，その目的の達成のために次の事業を行う。
　(1) 研究発表会，討論会の開催
　(2) 共同研究の実施
　(3) 研究資料の収集，配布
　(4) その他必要な事項

（部会員）
第４条　この部会は，農業農村工学会（旧農業土木学会）会員の中で，とくに土壌物理について研究しようとする者であって，この部会の趣旨に賛同し入会を希望する者を構成員とする。但し，農業農村工学会（旧農業土木学会）員以外で入会を希望するものについては，これを妨げない。

（役員）
第5条　この部会に次の役員を置く。
　(1)部会長（任期は２年）　１名
　(2)幹事　全国大学および研究機関より選出（若干名）
　(3)会計監査　２名

（幹事会）
第６条　この事業の円滑な運営を図るため，部会には幹事会を設ける。また，必要に応じて各種委員会を置くことができる。

（経費）
第７条　この部会の経費は，農業農村工学会（旧農業土木学会）研究部会交付金，会員の負担及び寄付金等による。

（事務局）
第8条　この部会の事務局は，部会長の所属機関内に置く。

付則

この規約は平成 15 年 7 月 9 日より発効する。
改訂：平成 19 年 10 月 14 日

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

2008年10月19日（日）

農業農村工学会土壌物理研究部会　事務局

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部会長　　　　取出　伸夫

事務局幹事　　渡辺　晋生

　　　　　　　井本　博美（東京大学）