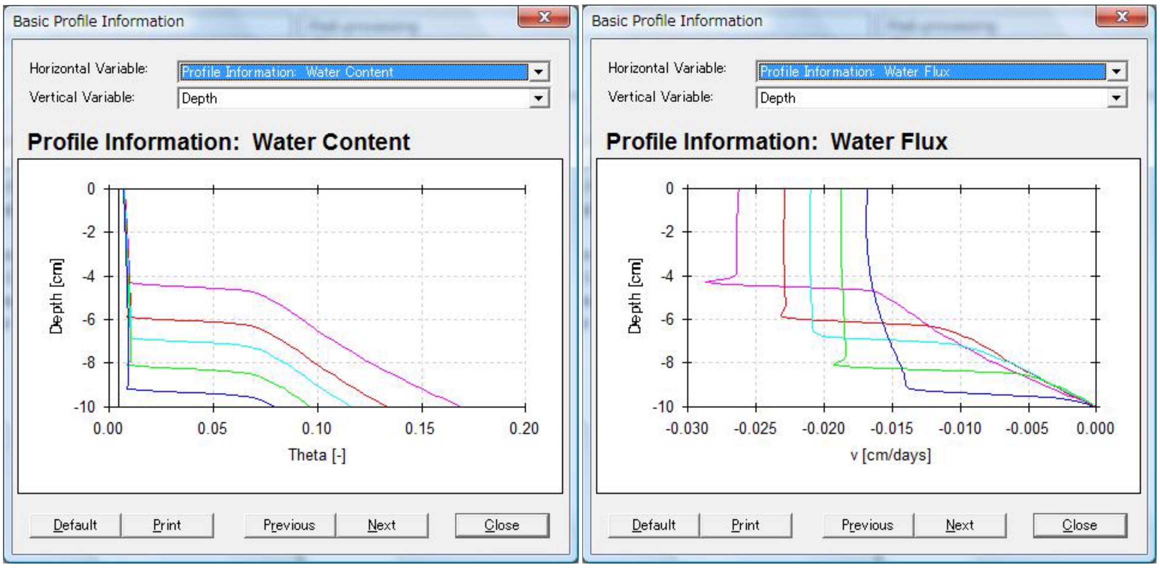
第 47 回　農業農村工学会　土壌物理研究部会　研究集会

HYDRUS-1D の新機能の紹介と今後の展開



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主催:農業農村工学会土壌物理研究部会

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HP1: A Coupled Numerical Code for Variably Saturated Water Flow, Solute Transport, and Biogeochemistry in Soil Systems

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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

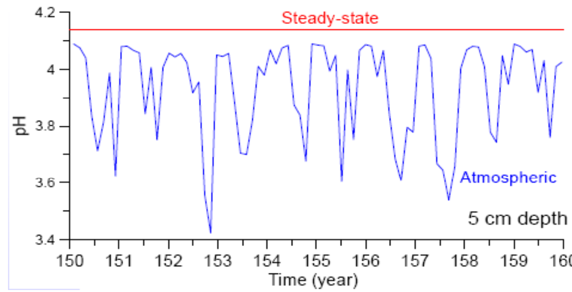
Cycling of major and trace elements in soil-plant systems

- 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*)

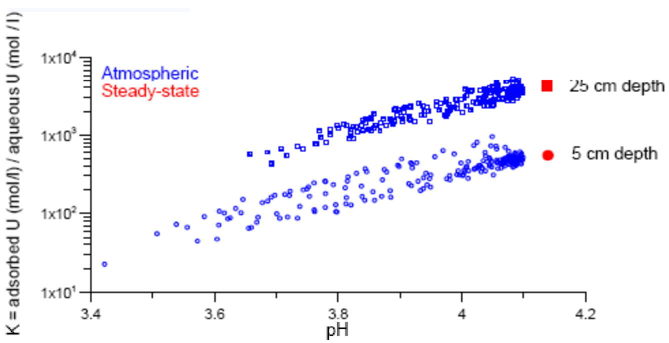


pH variations of soil water under the atmospheric condition:

- *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:

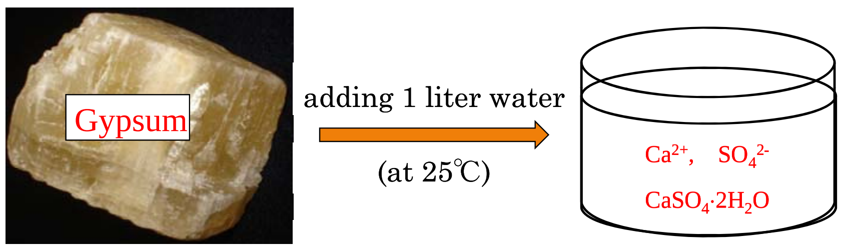
A computer program for biogeochemical reactions, based on the *law of mass action*.

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

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

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

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

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

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

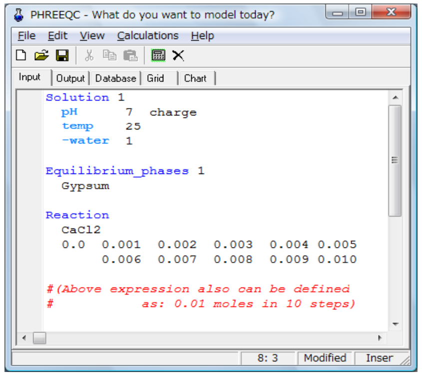
$$\Rightarrow \quad \Delta x = 0.00048 \quad (mol/l)$$

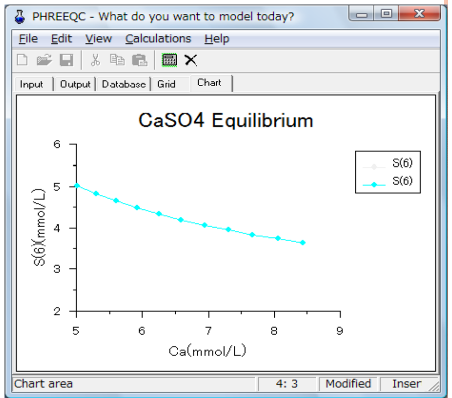
$$[Ca^{2+}]_{n-e} = 0.00601 - \Delta x = 0.00553 \quad (mol/l)$$

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

Results

Q 3: Using the PHREEQC code.





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

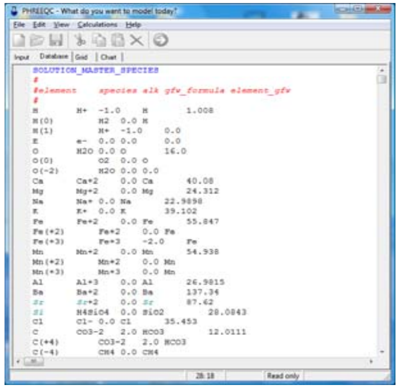
PHREEQC can simulate:

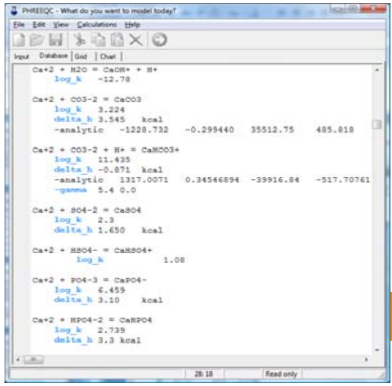
(*iii*) mixed equilibrium/kinetic reactions

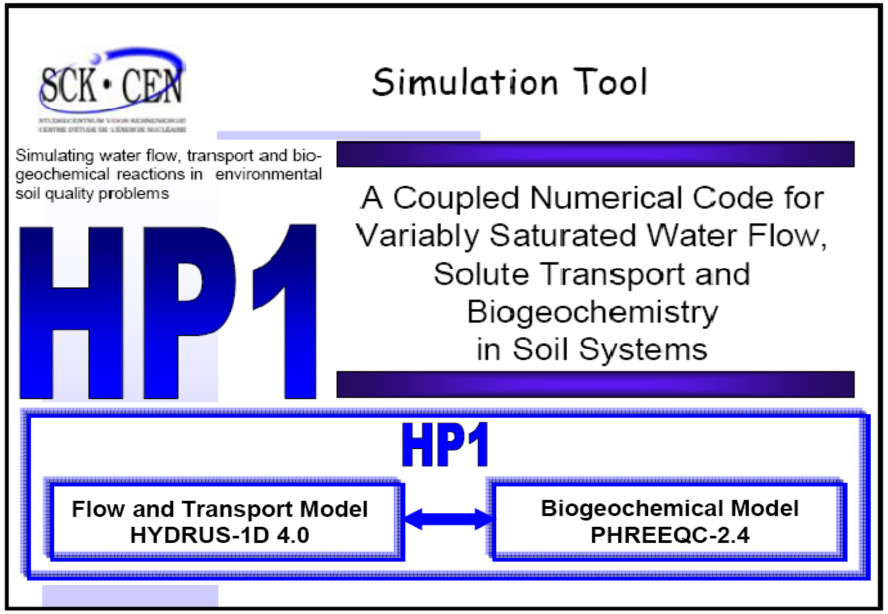
- chain reactions (modeled as kinetic type) including adsorbed phase (modeled as equilibrium type), etc.

PHREEQC: General description

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







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

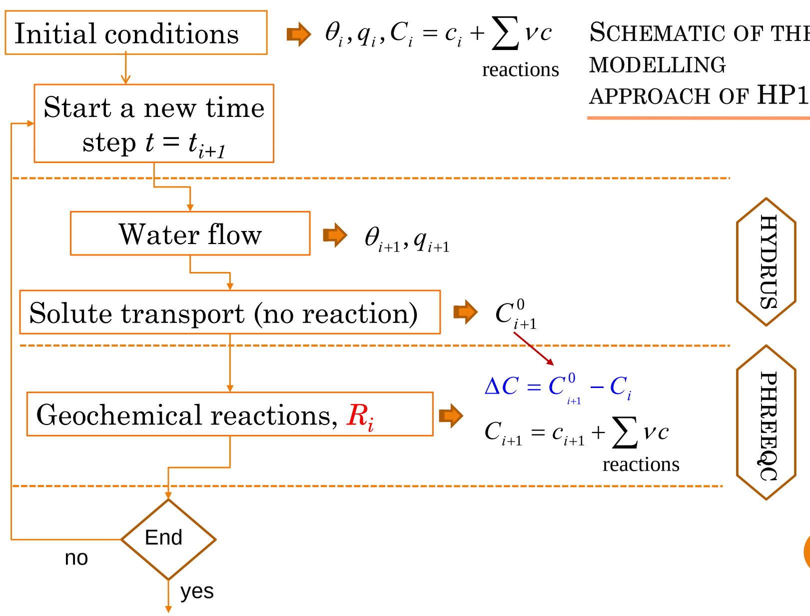
$$\frac{\partial \theta c_{l,i}}{\partial t} = \frac{\partial}{\partial x}\left(\theta D^w \frac{\partial c_{l,i}}{\partial x}\right) - q\frac{\partial c_{l,i}}{\partial x} - Sc_{r,i} + R_i$$

First

HYDRUS-1D
(physical transport part)

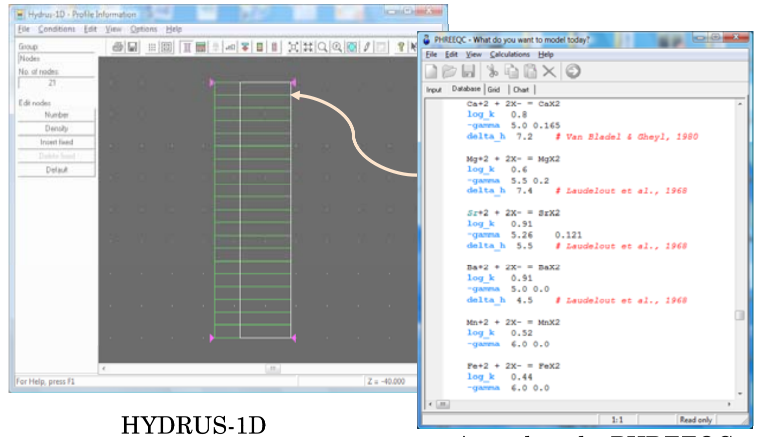
Second

PHREEQC
(geochemical reactions part)



SCHEMATIC OF THE MODELLING APPROACH OF HP1

HP1 coupling procedure



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.
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