New HYDRUS Modules for Simulating Preferential Flow, Colloid-Facilitated Solute Transport, and Various Biogeochemical Processes in Soils

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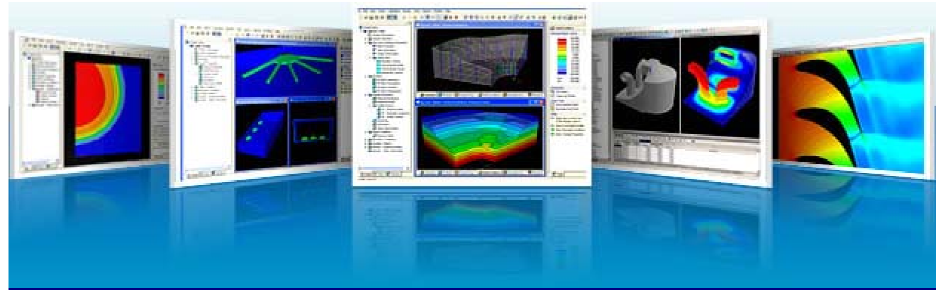


HYDRUS (1D/2D/3D)

Software for Simulating Water Flow and Solute Transport in One/Two/Three - Dimensional Variably-Saturated Soils Using Numerical Solutions

HYDRUS and its Modules

- HYDRUS + PHREEQC = HP1/2/3
  (hydrological + biogeochemical processes)
- HYDRUS + UNSATCHEM
  (hydrological + CO_2 + major ion processes)
- HYDRUS + Wetland (CW2D/CWM1)
  (biogeochem processes in constructed wetlands)
- HYDRUS + C-Ride
  (colloid-facilitated solute transport)
- HYDRUS + DualPerm
  (preferential water flow and solute transport)

HP1/2/3 (HYDRUS+PHREEQC)

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

HPx

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

HP1/2/3

Flow and transport model		Biogeochemical model
HYDRUS-1D 4.0 **HYDRUS (2D/3D) 2.x**	⟷	**PHREEQC-2.4**

HP1/2/3 (HYDRUS+PHREEQC)

HYDRUS-1D or HYDRUS (2D/3D):

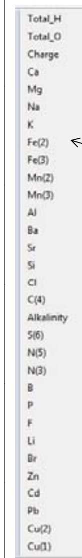
- Variably-Saturated Water Flow
- Solute Transport
- Heat Transport
- Gas Transport
- Root Water Uptake

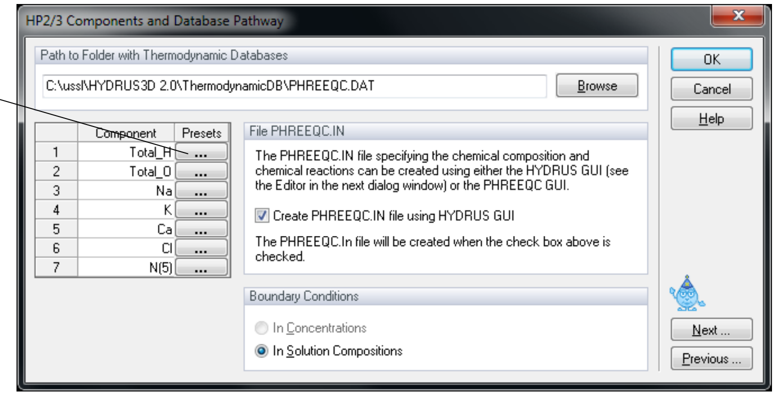
PHREEQC [Parkhurst and Appelo, 1999]:

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

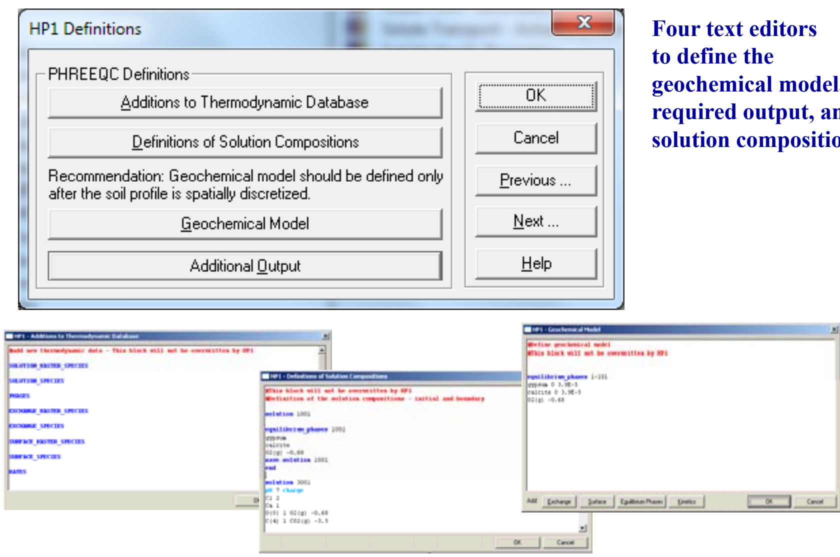
HYDRUS GUI for HP1/2/3





Jacques, D., and J. Šimůnek, Notes on the HP1 software – a coupled code for variably-saturated water flow, heat transport, solute transport and biogeochemistry in porous media, HP1 Version 2.2, *SCK•CEN-BLG-1068,* Waste and Disposal, SCK•CEN, Mol, Belgium, 114 pp., 2010.

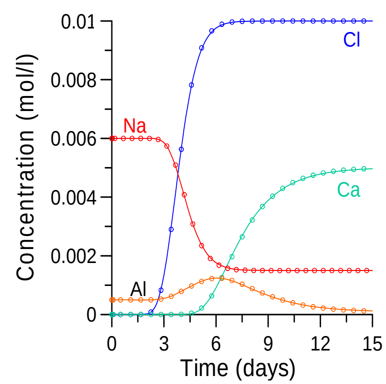
HYDRUS GUI for HP1/2/3

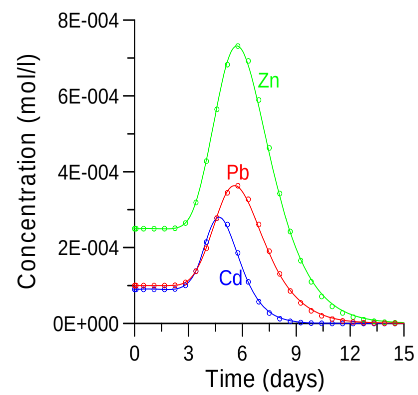


Four text editors to define the geochemical model, required output, and solution compositions

Transport and Cation Exchange Heavy Metals

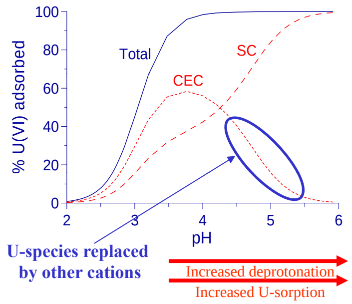
Major ions (Ca, Na, Al, Cl) and Heavy Metals (Zn, Pb, Cd)

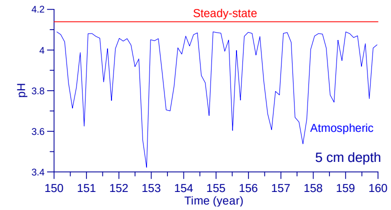




8-cm column is initially contaminated with heavy metals (in equilibrium with the cation exchanger). The column is then flushed with a solution ($CaCl_2$) without heavy metals.

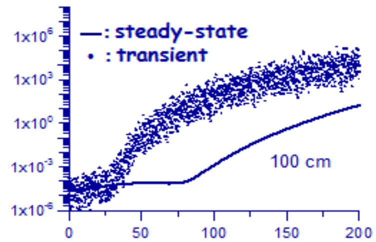
U-Transport in Agricultural Field Soils





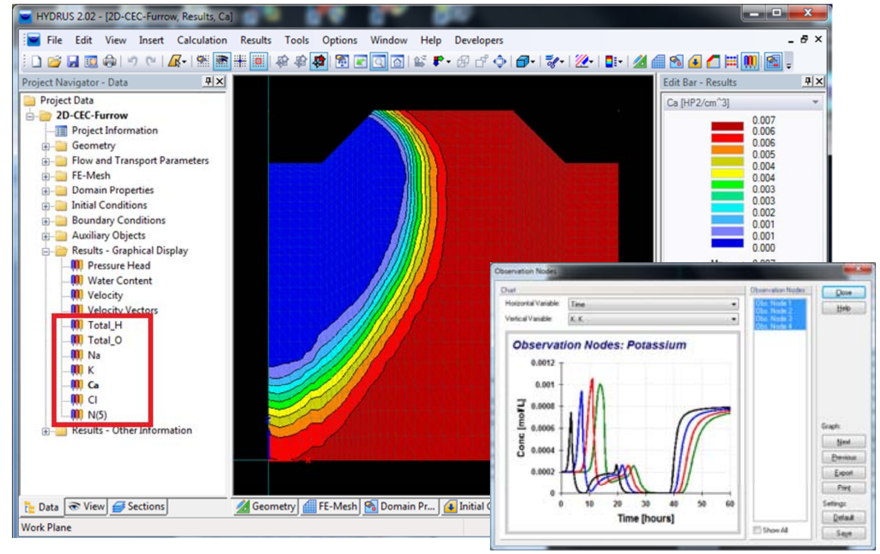
- ◆ Water content variations induce pH variations (dry soil => low pH)
- ◆ pH variations => variations in sorption potential (low pH => low sorption – higher mobility)

- ◆ **Aqueous speciation reactions**
  C, Ca, Cl, F, H, K, Mg, N(5), Na, O(0), O(-2), P, S(6), U(6)
- ◆ **Multi-site cation exchange reactions**
  - Related to amount of organic matter
  - Increases with increasing pH
  - UO_2^{2+} adsorbs
- ◆ **Surface complexation reactions**
  - Specific binding to charged surfaces (≡FeOH)
  - Related to amount of Fe-oxides

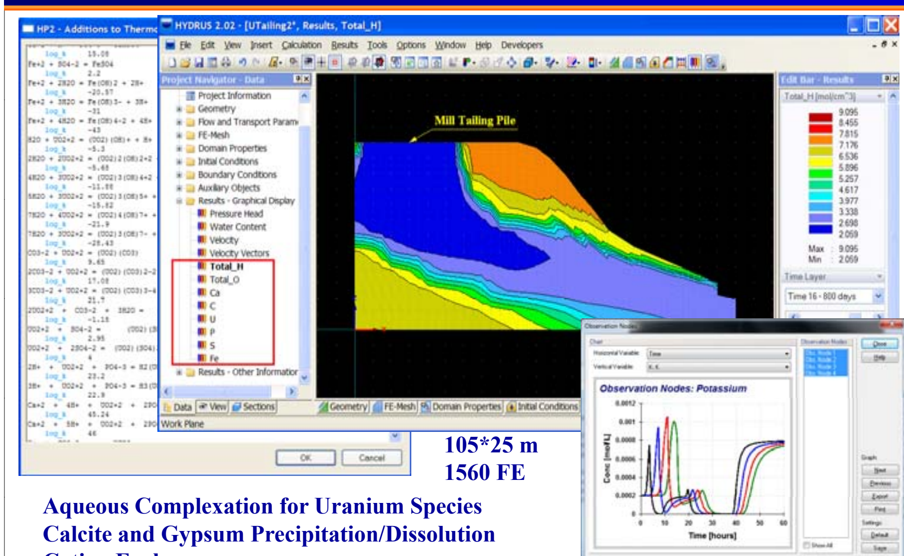


Jacques et al., VZJ, 2008.

HP2 – Reclamation of a Sodic Soil



Uranium Transport from Mill Tailing Pile



105*25 m
1560 FE

Aqueous Complexation for Uranium Species
Calcite and Gypsum Precipitation/Dissolution
Cation Exchange

HP1 Examples

- ◆ Transport of Heavy Metals (Zn^{2+}, Pb^{2+}, and Cd^{2+}) subject to a multiple pH-dependent Cation Exchange
- ◆ Transport and mineral dissolution of Amorphous SiO_2 and Gibbsite
- ◆ Infiltration of a Hyperalkaline Solution in a clay sample (kinetic precipitation-dissolution of kaolinite, illite, quartz, calcite, dolomite, gypsum, hydrotalcite, and sepiolite)
- ◆ Kinetic biodegradation of NTA (biomass, cobalt)
- ◆ Long-term Uranium transport following mineral phosphorus fertilization (pH-dependent surface complexation and cation exchange)
- ◆ Transport of Explosives, such as TNT and RDX
- ◆ Property Changes (porosity/conductivity) due to precipitation/ dissolution reactions

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  (processes in constructed wetlands)
- ◆ HYDRUS + C-Ride
  (colloid-facilitated solute transport)
- ◆ HYDRUS + DualPerm
  (preferential water flow and solute transport)

HYDRUS + UNSATCHEM

- ◆ **HYDRUS and HYDRUS (2D/3D)**
  - Variably-Saturated Water Flow
  - Solute Transport
  - Heat Transport
  - Root Water Uptake
- ◆ **UNSATCHEM** (Šimůnek et al., 1996)
  - Carbon Dioxide Transport
  - Major Ion Chemistry
    - Cation Exchange
    - Precipitation-Dissolution (instantaneous and kinetic)
    - Aqueous Complexation

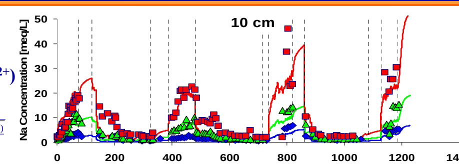
UNSATCHEM Module

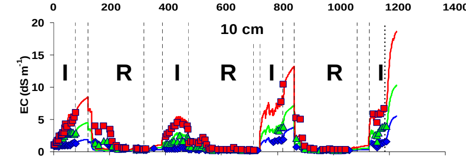
1	Aqueous Components	7	Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, Cl^{-}, NO_3^{-}
2	Complexed Species	10	$CaCO_3^{o}$, $CaHCO_3^{+}$, $CaSO_4^{o}$, $MgCO_3^{o}$, $MgHCO_3^{+}$, $MgSO_4^{o}$, $NaCO_3^{-}$, $NaHCO_3^{o}$, $NaSO_4^{-}$, KSO_4^{-}
3	Precipitated Species	6	$CaCO_3$, $CaSO_4 \cdot 2H_2O$, $CaMg(CO_3)_2$, $MgCO_3 \cdot 3H_2O$, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$, $Mg_2Si_3O_{7.5}(OH) \cdot 3H_2O$
4	Sorbed Species (exchangeable)	4	XCa, XMg, XNa, XK
5	CO_2-H_2O Species	7	P_{CO2}, $H_2CO_3^{*}$, CO_3^{2-}, HCO_3^{-}, H^{+}, OH^{-}, H_2O
6	Silica Species	3	H_4SiO_4, $H_3SiO_4^{-}$, $H_2SiO_4^{2-}$

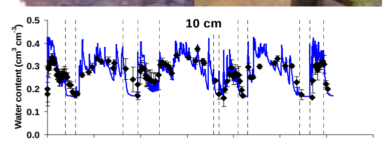
Kinetic reactions: calcite precipitation/dissolution, dolomite dissolution
Activity coefficients: extended Debye-Hückel equations, Pitzer expressions

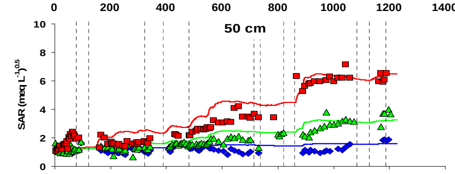
UNSATCHEM - Lysimeter Study

To evaluate the effectiveness of HYDRUS to predict:
- ◆ Water content and fluxes
- ◆ Concentration of individual cations (e.g., Ca^{2+}, Mg^{2+})
- ◆ Overall salinity (Electrical conductivity – *EC*)
- ◆ Sodium Adsorption Ratio (*SAR*) $SAR = \frac{(Na^+)}{\sqrt{\frac{(Ca^{2+}+Mg^{2+})}{2}}}$
- ◆ Exchangeable Sodium Percentage (*ESP*)





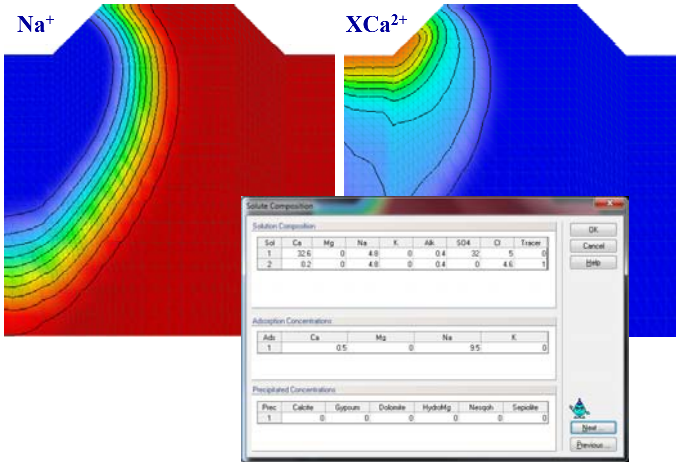


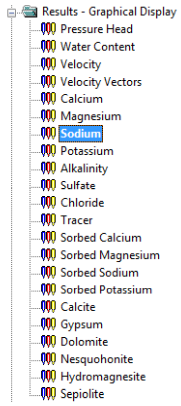


Gonçalves, M. C., J. Šimůnek, T. B. Ramos, J. C. Martins, M. J. Neves, and F. P. Pires, Multicomponent solute transport in soil lysimeters irrigated with waters of different quality, *Water Resources Research*, *42*, 17 pp., 2006.
Ramos, T. B., J. Šimůnek, M. C. Gonçalves, J. C. Martins, A. Prazeres, N. L. Castanheira, and L. S. Pereira, Field evaluation of a multicomponent solute transport model in soils irrigated with saline waters, *J. of Hydrology*, *407*(1-4), 129-144, 2011.

UNSATCHEM-2D Module

Major Ion Chemistry Module





Šimůnek, J., and D. L. Suarez, Two-dimensional transport model for variably saturated porous media with major ion chemistry, *Water Resources Research*, *30*(4), 1115-1133, 1994.

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Wetland Module

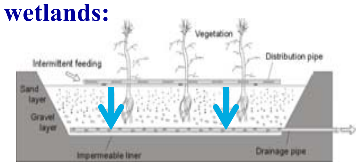
Constructed Wetlands (CWs) or wetland treatment systems

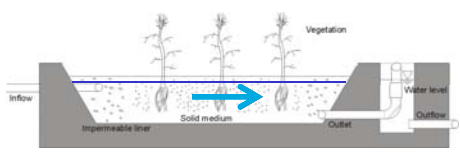
- designed to improve water quality
- use the same processes that occur in natural wetlands but have the flexibility of being constructed
- effective in treating organic matter, nitrogen, phosphorus, and additionally for decreasing the concentrations of heavy metals, organic chemicals, and pathogens

CW2D : aerobic and anoxic processes for organic matter, nitrogen and phosphorus (Langergraber and Šimůnek, 2005)

CWM1: aerobic, anoxic and anaerobic processes for organic matter, nitrogen and sulphur (Langergraber et al., 2005)

Subsurface Vertical (CW2D) and Horizontal (CWM1) flow constructed wetlands:



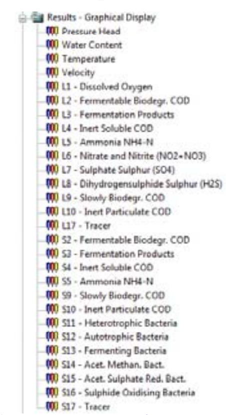


Wetland Modules: Components

CW2D : aerobic and anoxic processes for organic matter, nitrogen and phosphorus
CWM1: aerobic, anoxic and anaerobic processes for organic matter, nitrogen and sulphur

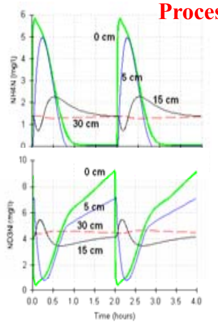
Components:

CW2D (Langergraber and Šimůnek, 2005)	CWM1 (Langergraber et al., 2009b)
Organic matter, nitrogen, phosphorus	**Organic matter, nitrogen, sulphur**
CW2D components	**Soluble components**
1. **SO**: *Dissolved oxygen, O2.*	1. **SO**: *Dissolved oxygen, O2.*
2. **CR**: *Readily biodegradable soluble COD.*	2. **SF**: *Fermentable, readily biodegradable soluble COD.*
3. **CS**: *Slowly biodegradable soluble COD.*	3. **SA**: *Fermentation products as acetate.*
4. **CI**: *Inert soluble COD.*	4. **SI**: *Inert soluble COD.*
5. **XH**: *Heterotrophic bacteria*	5. **SNH**: *Ammonium and ammonia nitrogen.*
6. **XANs**: *Autotrophic ammonia oxidizing bacteria (Nitrosomonas spp.)*	6. **SNO**: *Nitrate and nitrite nitrogen.*
7. **XANb**: *Autotrophic nitrite oxidizing bacteria (Nitrobacter spp.)*	7. **SSO4**: *Sulphate sulphur.*
8. **NH4N**: *Ammonium and ammonia nitrogen.*	8. **SH2S**: *Dihydrogensulphide sulphur.*
9. **NO2N**: *Nitrite nitrogen.*	**Particulate components**
10. **NO3N**: *Nitrate nitrogen.*	9. **XS**: *Slowly biodegradable particulate COD.*
11. **N2**: *Elemental nitrogen.*	10. **XI**: *Inert particulate COD.*
12. **PO4P**: *Phosphate phosphorus*	11. **XH**: *Heterotrophic bacteria.*
	12. **XA**: *Autotrophic nitrifying bacteria.*
	13. **XFB**: *Fermenting bacteria.*
Organic nitrogen and organic phosphorus are modeled as part of the COD.	14. **XAMB**: *Acetotrophic methanogenic bacteria.*
Nitrification is modeled as a two-step process.	15. **XASRB**: *Acetotrophic sulphate reducing bacteria.*
Bacteria are assumed to be immobile.	16. **XSOB**: *Sulphide oxidizing bacteria.*
It is generally assumed that all components except bacteria are soluble.	Organic nitrogen and organic phosphorus are modeled as part of the COD.



Langergraber, G., and J. Šimůnek, The Multi-component Reactive Transport Module CW2D for Constructed Wetlands for the HYDRUS Software Package, Manual – Version 1.0, *HYDRUS Software Series 2*, Department of Environmental Sciences, University of California Riverside, Riverside, CA, 72 pp., 2006.
Langergraber, G., D. Rousseau, J. Garcia, and J. Mean, CWM1 - A general model to describe biokinetic processes in subsurface flow constructed wetlands, *Water Science Technology*, 59(9), 1687-1697, 2009.

Wetland Modules: Processes



Processes:

CW2D (Langergraber and Šimůnek, 2005)

Heterotrophic bacteria:
1. *Hydrolysis:* conversion of CS into CR.
2. *Aerobic growth of XH on CR* (mineralization of organic matter).
3. *Anoxic growth of XH on CR* (denitrification on NO2N).
4. *Anoxic growth of XH on CR* (denitrification on NO3N).
5. *Lysis of XH*.

Autotrophic bacteria:
6. *Aerobic growth of XANs on SNH* (ammonium oxidation).
7. *Lysis of XANs*.
8. *Aerobic growth of XANb on SNH* (nitrite oxidation).
9. *Lysis of XANb*.

CWM1 (Langergraber et al., 2009b)

Heterotrophic bacteria:
1. *Hydrolysis*: conversion of XS into SF.
2. *Aerobic growth of XH on SF* (mineralization of organic matter).
3. *Aerobic growth of XH on SA* (mineralization of organic matter).
4. *Anoxic growth of XH on SF* (denitrification).
5. *Anoxic growth of XH on SA* (denitrification).
6. *Lysis of XH*.

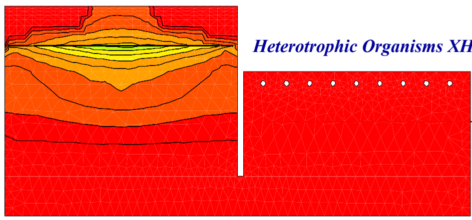
Autotrophic bacteria:
7. Aerobic growth of XA on SNH (nitrification).
8. Lysis of XA.

Fermenting bacteria:
9. Growth of XFB (fermentation).
10. Lysis of XFB.

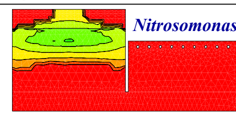
Acetotrophic methanogenic bacteria:
11. Growth of XAMB: Anaerobic growth of acetotrophic, methanogenic bacteria XAMB on acetate SA.
12. Lysis of XAMB.

Acetotrophic sulphate reducing bacteria:
13. Growth of XASRB: Anaerobic growth of acetotrophic, sulphate reducing bacteria.
14. Lysis of XASRB.

Sulphide oxidizing bacteria:
15. Aerobic growth of XSOB on SH2S: The opposite process to process 13, the oxidation of SH2S to SSO4.
16. Anoxic growth of XSOB on SH2S: Similar to process 15 but under anoxic conditions.
17. Lysis of XSOB.



Heterotrophic Organisms XH



Nitrosomonas XANs

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- **HYDRUS + C-Ride**
  (colloid-facilitated solute transport)
- HYDRUS + DualPerm
  (preferential water flow and solute transport)

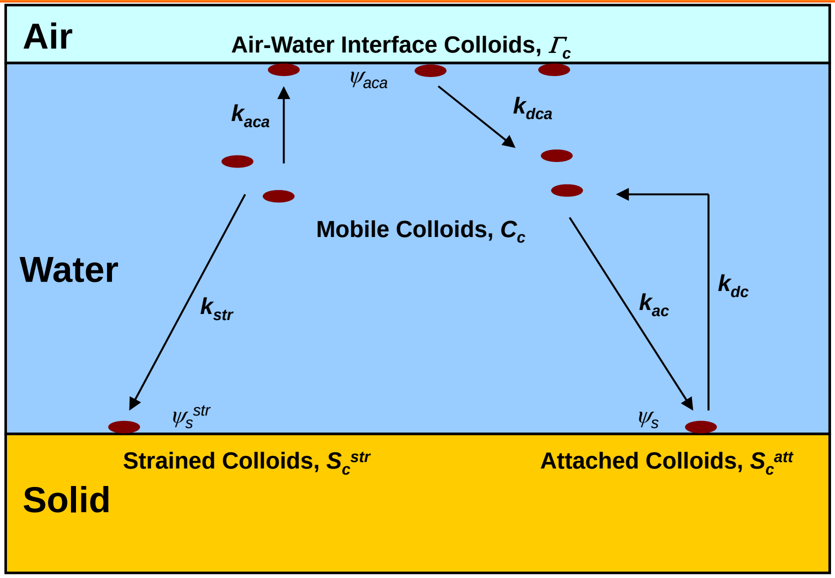
Colloid-Facilitated Solute Transport

- **Many contaminants should be relatively immobile in the subsurface since under normal conditions they are strongly sorbed to soil**
- **They can also sorb to colloids which often move at rates similar or faster as non-sorbing tracers**
- **Experimental evidence exists that many contaminants are transported not only in a dissolved state by water, but also sorbed to moving colloids.**
- **Examples: heavy metals, radionuclides, pesticides, viruses, pharmaceuticals, hormones, and other contaminants**

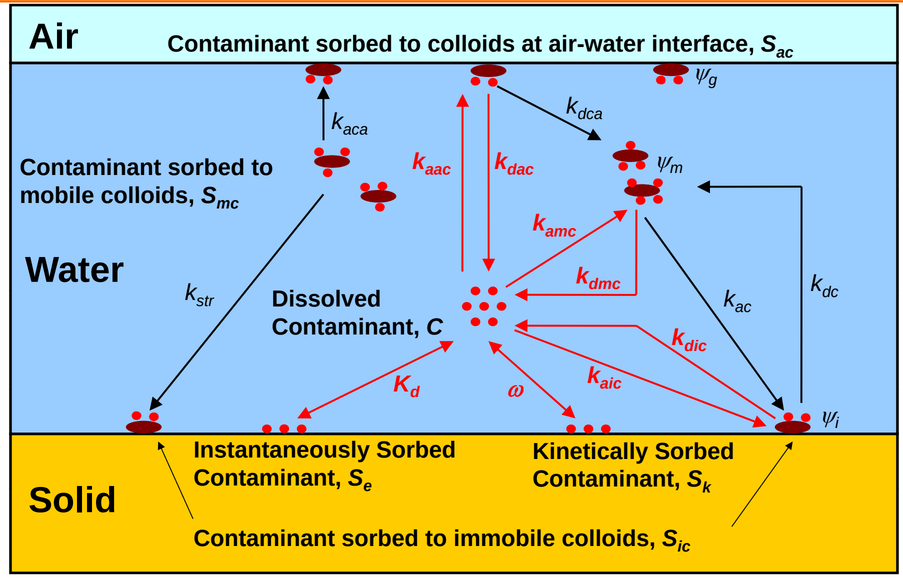
HYDRUS + C-Ride

- **HYDRUS and HYDRUS (2D/3D)**
  - Variably-Saturated Water Flow
  - Solute Transport
  - Heat Transport
  - Root Water Uptake
- **C-Ride** (Šimůnek et al., 2006)
  - Particle Transport
    - colloids, bacteria, viruses, nanoparticles
    - attachment/detachment, straining, blocking
  - Colloid-Facilitated Solute Transport
    - transport of solutes attached to particles

Colloid, Virus, and Bacteria Transport



Colloid-Facilitated Solute Transport



Colloid-Facilitated Solute Transport

Mass Balance of Total Contaminant:

$$\frac{\partial \theta C}{\partial t} + \rho\frac{\partial S_e}{\partial t} + \rho\frac{\partial S_k}{\partial t} + \frac{\partial \theta_w C_c S_{mc}}{\partial t} + \rho\frac{\partial S_c S_{ic}}{\partial t} + \frac{\partial A_{aw}\Gamma_c S_{ac}}{\partial t}$$

$$= \frac{\partial}{\partial x}\left(\theta D \frac{\partial C}{\partial x}\right) - \frac{\partial qC}{\partial x} + \frac{\partial}{\partial x}\left(\theta_w S_{mc} D_c \frac{\partial C_c}{\partial x}\right) - \frac{\partial q_c C_c S_{mc}}{\partial x} + R$$

Left-hand side sums the Mass of Contaminant:

- in the liquid phase
- sorbed instantaneously and kinetically to the solid phase
- sorbed to mobile and immobile (attached to solid phase or air–water interface) colloids

Right-hand side considers various Spatial Mass Fluxes

- dispersion and advective transport of the dissolved contaminant
- dispersion and advective transport of contaminant sorbed to mobile colloids

and Transformation/Reaction (e.g., degradation).

Colloid-Facilitated Solute Transport

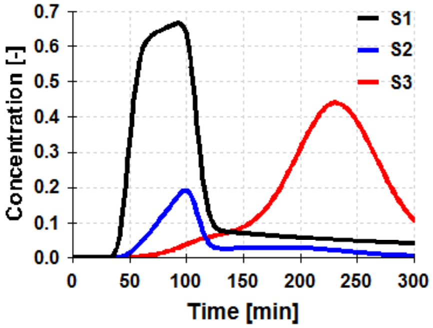
System of coupled equations (solved numerically):

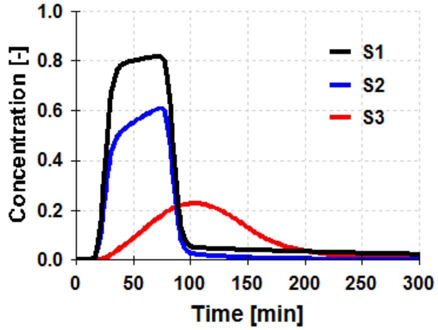
a) Five Partial Differential Equations
- total mass of contaminant
- mass of contaminant sorbed kinetically to solid phase
- mass of contaminant sorbed to mobile colloids
- mass of contaminant sorbed to attached colloids
- mass of contaminant sorbed to strained colloids

b) One Algebraic Equation
- mass of contaminant sorbed instantaneously to solid phase (adsorption isotherm)

Colloid-Facilitated Solute Transport

C-Ride Module





Breakthrough curves for colloids (black line), solute sorbed to colloids (blue line), and solute (red line):

Left: solute and colloids are applied **independently**

Right: solute is **attached** initially to colloids

The Retardation Factor for colloids is equal to 1 and for solute to 4

Unit input concentrations.

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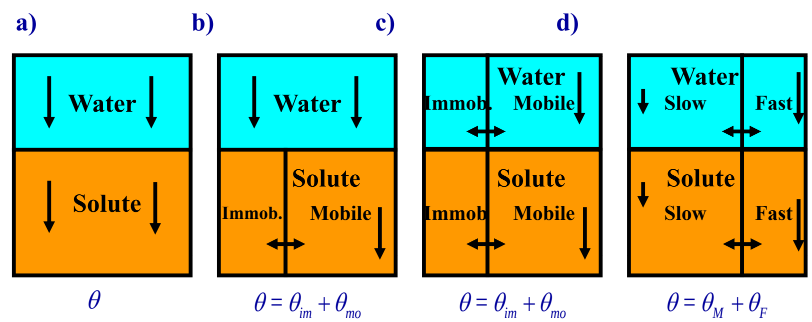
Preferential Flow and Transport

Fractured Rock

Macroporous Soil

The DualPerm Module

Physical Nonequilibrium Solute Transport Models in DualPerm



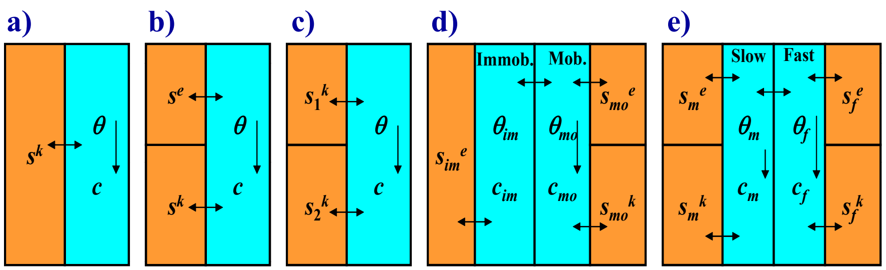
a) Uniform Flow

b) Mobile-Immobile Water

c) Dual-Porosity (Šimůnek et al., 2003)

d) Dual-Permeability (Gerke and van Genuchten, 1993)

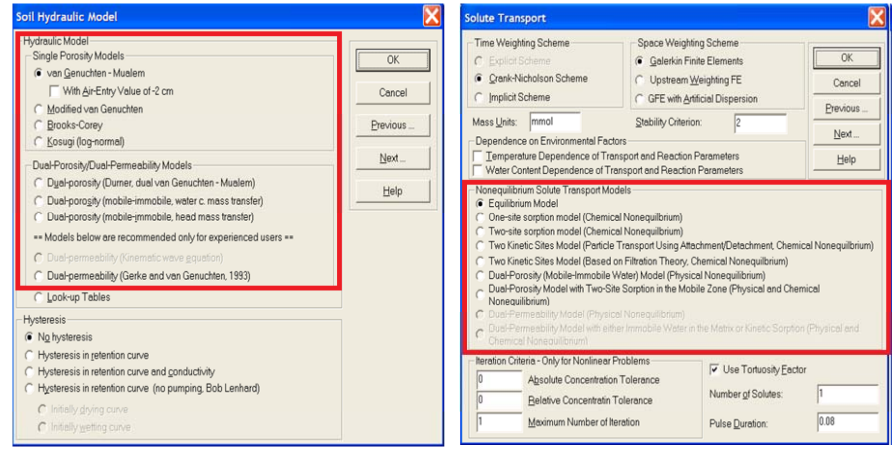
Chemical Nonequilibrium Solute Transport Models in DualPerm



a) One-Site Kinetic Model
b) Two-Site Model (kinetic and instantaneous sorption)
c) Two Kinetic Sites Model
(particle transport, e.g., colloids, viruses, bacteria)
d) Dual-Porosity with One Kinetic Site Model
e) Dual-permeability with Two-Site Model

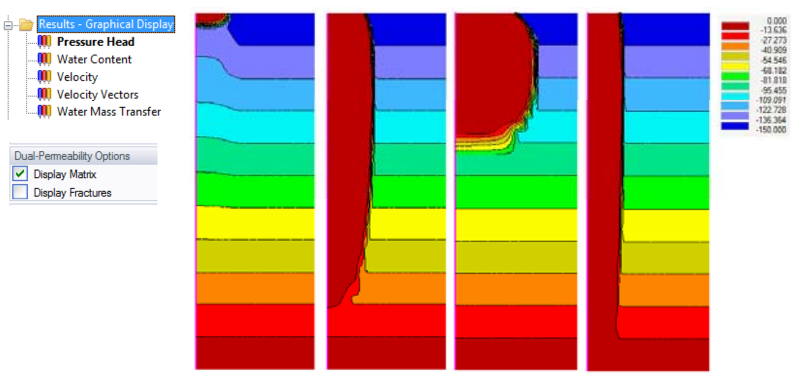
Nonequilibrium Models in the HYDRUS GUI

Variably-Saturated Water Flow **Solute Transport**



The DualPerm Module

Water flow and Solute Transport in Dual-Permeability Variably-Saturated Porous Media

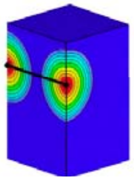


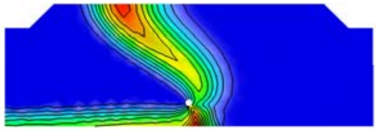
Pressure head profiles for the matrix (left), isotropic fracture, and fracture with K_x^A/K_z^A=10, and fracture with K_x^A/K_z^A=0.1 (right).

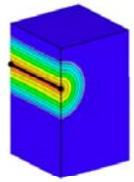
HYDRUS and its Future Modules?

- HYDRUS + Overland Flow
  (surface runoff and overland flow)
- HYDRUS + Global Optimization
  (genetic algorithm, AMALGAM, …)
- HYDRUS + MODFLOW
  (hydrological processes at a large scale)
- HYDRUS + Soil Mechanical Stresses
  (effects of hydrological processes on slope stability)
- HYDRUS + Freezing, Meteo (atmosphere)…

Questions and Suggestions?







Thank you for your attention