

The HYDRUS-PHREEQC Multicomponent Transport Model For Variably-Saturated Porous Media: Code Verification and Application

Diederik Jacques¹, Jirka Šimůnek², Dirk Mallants¹ and Martinus Th. van Genuchten²

¹Waste and Disposal Department, SCK•CEN, djacques@sckcen.be,
dmallant@sckcen.be, Mol, Belgium

²George E. Brown, Jr. Salinity Laboratory, USDA, ARS, jsimunek@ussl.ars.usda.gov,
rvang@ussl.ars.usda.gov, Riverside, CA, USA

ABSTRACT

A new coupled model for multicomponent reactive transport during transient variably-saturated flow is presented. The model combines two comprehensive existing models: HYDRUS-1D and PHREEQC. HYDRUS-1D is a one-dimensional finite element model simulating the movement of water, heat and multiple solutes in variably-saturated heterogeneous or layered soils subject to a variety of atmospheric and other boundary conditions. PHREEQC is a computer program simulating the behavior of complex chemical systems, including such reactions as speciation, ion exchange, surface complexation, and mineral precipitation/dissolution. The accuracy of the coupled HYDRUS1D-PHREEQC model was verified by comparing simulation results with calculations obtained with an independent model (CRUNCH, using both the operator splitting and global implicit coupling modes) for two steady-state flow problems. One problem considered the transport of heavy metals in a layered soil profile having a pH-dependent cation exchange complex. Another problem simulated the intrusion of a high-pH solution (pH 13) into a compacted clay core leading to kinetic dissolution of primary minerals and precipitation of secondary minerals. Simulation results of HYDRUS1D-PHREEQC were in close agreement with those by CRUNCH for both problems. We illustrate the possibilities of the new code by predicting the long-term leaching of heavy metals (Cd, Zn, and Pb) in a contaminated soil profile. The example shows several levels of complexity that can be considered with the coupled multicomponent transport model.

INTRODUCTION

The migration of many naturally occurring elements and contaminants in the subsurface is affected by a multitude of complex, interactive physical, chemical, mineralogical and biological processes. Cycles of precipitation and evapotranspiration largely determine if contaminants remain near the soil surface. Changes in the chemical composition or pH of the soil solution may impact the retention of heavy metals on organic matter or iron oxides. Dissolution and precipitation of minerals generally buffer the transport of a solution with a different pH through the soil profile. Simulation of these and related processes requires a coupled reactive transport code that integrates the physical processes of water flow and advective-dispersive solute transport with a range of biogeochemical processes.

In this paper we describe a new reactive transport code based on the coupling of two existing models: HYDRUS-1D (Šimůnek et al., 1998) simulating water flow and solute transport, and PHREEQC (Parkhurst and Appelo, 1999) considering speciation and other geochemical reactions. The combined HYDRUS1D-PHREEQC model allows one to simultaneously simulate variably-saturated transient water flow, multicomponent solute transport, speciation and geochemical processes, including a variety of mixed equilibrium and kinetic reactions. Simulations will be compared with results obtained with a different reactive transport model, CRUNCH (based on GIMRT/OS3D, Steefel and Yabuski, 1996), for two benchmark problems. One problem is limited to chemical speciation and cation exchange, while the second problem also involves dissolution and precipitation of minerals. The effect of using a global implicit coupling method versus a sequential non-iterative approach is assessed. The new capabilities of HYDRUS1D-PHREEQC are demonstrated by simulating heavy metal transport under atmospheric boundary conditions.

THE COMBINED HYDRUS1D – PHREEQC MODEL

To simulate the transport of multiple elements interacting with each other and the soil solid phase for different flow situations, the HYDRUS-1D water flow and solute transport model (Šimůnek et al., 1998) was coupled with the PHREEQC geochemical speciation model (Parkhurst and Appelo, 1999). Water flow and solute transport in HYDRUS-1D are described with the Richards and advection-dispersion equations, respectively. The code can simulate a variety of one-dimensional flow and transport scenarios, ranging from relatively simple steady-state problems, to more complex problems involving time-variable atmospheric boundary conditions, including evaporation and root water uptake. Geochemical reactions are not modeled with HYDRUS-1D. The PHREEQC geochemical speciation model considers aqueous speciation, gas, aqueous, and mineral equilibrium, oxidation-reduction reactions, and solid-solution, surface-complexation, ion-exchange and kinetic reactions. The HYDRUS-1D and PHREEQC models are coupled using a non-iterative operator splitting approach (SNIA), which first solves the physical part of the problem (water flow and solute transport) and then the geochemical part.

BENCHMARK AND EXAMPLE PROBLEMS

The CRUNCH model

The combined HYDRUS1D-PHREEQC model was tested against a different computer program, CRUNCH, for modeling multicomponent reactive transport in porous media. CRUNCH is based on the GIMRT/OS3D package (Steefel and Yabuski, 1996, Steefel, 2000). The geochemical reactions and transport in CRUNCH are coupled in one of two ways: (1) a global implicit approach (GIMRT) solving simultaneously the transport and reaction equations, or (2) SNIA. GIMRT generally leads to smaller numerical errors. A comparison of HYDRUS1D-PHREEQC and CRUNCH-GIMRT allows one to assess numerical discretization errors of the SNIA coupling as a function of the maximum Courant number Cr .

Heavy metal transport with a pH-dependent cation exchange complex

The first benchmark problem considers the transport of several major cations (Na, K, Ca, Mg) and three heavy metals (Cd, Zn, Pb) through a 50-cm deep multi-layered soil profile having different soil hydraulic properties and cation exchange capacities (CEC). Assuming that the CEC is associated solely with organic matter, it increases significantly with increasing pH due to the acid base properties of its functional groups. This behavior is represented by a multi-site cation exchange complex consisting of six sites, each having a different selectivity coefficient for the exchange of protons (see Appelo et al., 1998, for details). The top 28 cm of the soil was assumed to be contaminated with the three metals (initial pH 8.5), while an acid metal-free solution (pH 3) infiltrated into the soil. Flow was assumed to be steady at a constant flux of 0.05 cm day^{-1} , which causes the soil profile to be unsaturated (volumetric water content values varied between 0.37

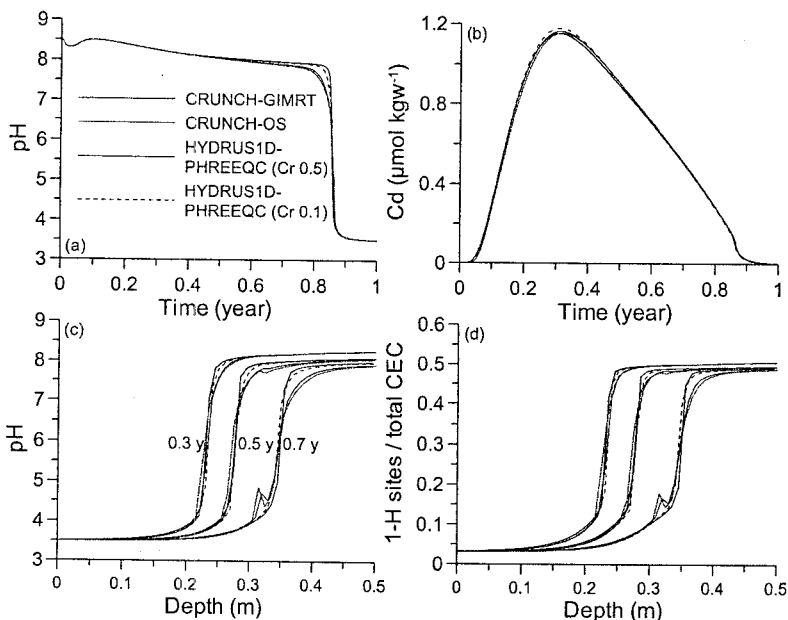


Figure 1. Selected simulation results for cation and heavy metal transport with a pH-dependent cation exchange complex: (a) and (b) pH and Cd concentration in outflow at 50 cm depth, (c) and (d) distributions versus depth of pH and fraction of deprotonated sites after 0.3, 0.5, and 0.7 y.

Flow was assumed to be steady at a constant flux of 0.05 cm day^{-1} , which causes the soil profile to be unsaturated (volumetric water content values varied between 0.37

and 0.15). The dispersivity and diffusion coefficient were taken to be 0.05 m and $9.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$; respectively.

Figure 1 shows selected results for simulations with CRUNCH-GIMRT, CRUNCH-SNIA (*Cr* of 0.5), and HYDRUS1D-PHREEQC (*Cr* of 0.5 and 0.1). Infiltration of the low-pH solution causes an increase in the number of protonated sites on the cation exchange complex (Figure 1c and d), leading to leaching of the heavy metals. Cd leaching peaks after about 0.3 y (Figure 1b), with most Cd leached from the profile after 1 y.

Results obtained with CRUNCH-SNIA and HYDRUS1D-PHREEQC using *Cr* = 0.5 showed very good agreement, especially for the outflow curves. The SNIA approach with *Cr* = 0.5 produced somewhat more numerical dispersion as compared to simulations using the global implicit approach (CRUNCH-GIMRT), such as in the pH outflow curve and the different profiles after 0.7 y. Reducing *Cr* to 0.1 in HYDRUS1D-PHREEQC produced very good agreement with CRUNCH-GIMRT.

Infiltration of a hyperalkaline plume solution in a clay sample

Concrete is a key construction or backfill material in engineered deep disposal sites for nuclear waste in stable host rocks. Concrete may produce solutions with high Na and K concentrations and a pH larger than 13. Diffusion of this high-pH solution in the surrounding host rock could induce several geochemical reactions such as cation exchange, dissolution of primary minerals and subsequent precipitation of secondary minerals. The second benchmark problem is based on a study of Adler (2001) to model the

infiltration of a hyperalkaline solution in an Opalinus Clay core. Primary minerals of the Opalinus Clay are kaolinite, illite, quartz, calcite, dolomite, gypsum. Kinetic dissolution of the primary minerals, caused by the increase in pH, is described using a 'transition state' based dissolution model (Aagaard and Helgeson, 1981). Dissolution reactions and kinetic parameters are given by Adler (2001). Two secondary minerals, sepiolite and hydrotalcite, were included in the model. Na, K, Ca, and Mg were assumed to be subject to cation exchange reactions, with Opalinus Clay having a CEC of 120 meq per kg rock. Infiltration in a 7.4 cm long clay core was simulated for a period of 1.1 year. The sample had a porosity of 0.13 and was subjected to a constant water flux of $2.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The diffusion coefficient was assumed to be $0.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, and the dispersivity 0 m.

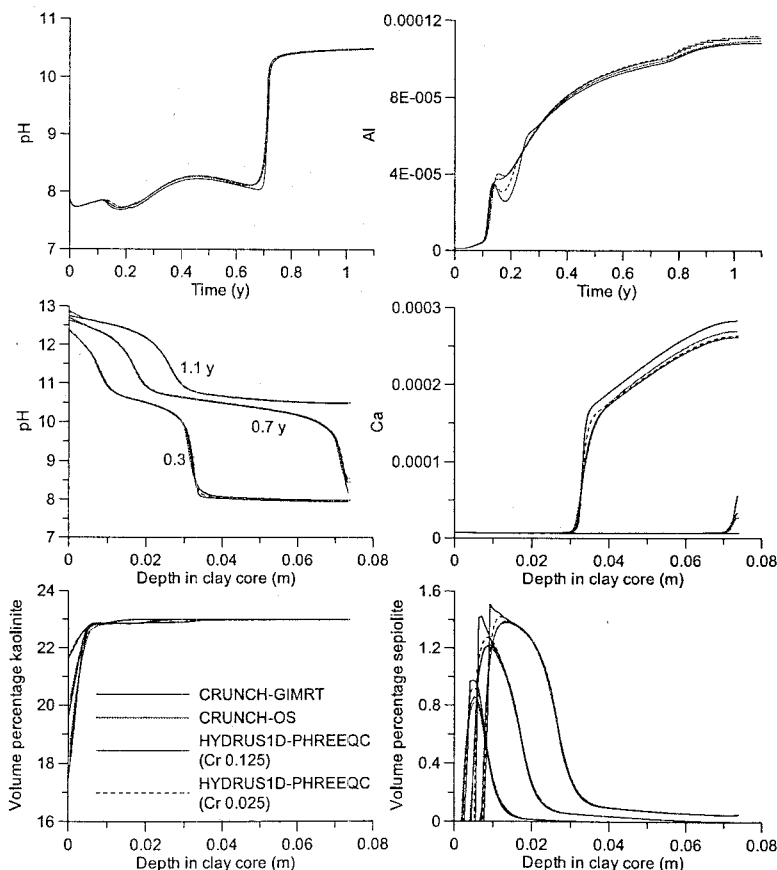


Figure 2. Selected outflow curves and distributions versus depth after 0.3, 0.7, and 1.1 y of infiltration of a high pH solution in an Opalinus Clay core.

Simulations were again carried out with the three models, using *Cr* values of 0.125 and 0.025 in HYDRUS1D-PHREEQC. Figure 2 shows selected outflow curves and sample profiles after 0.3, 0.7, and 1.1 y. Transport through the

Opalinus clay core is governed by a sequence of reactions such as those typical of cation exchange chromatography in a soil core, and including dolomite, quartz and kaolinite dissolution followed by calcite, sepiolite and hydrotalcite dissolution. We refer to Adler (2001) for a detailed discussion of these reactions, which is outside the scope of this paper.

Close agreement was found between simulations with CRUNCH-GIMRT, CRUNCH-SNIA and HYDRUS1D-PHREEQC. Results obtained with the sequential non-iterative coupling method differed somewhat from the global implicit method (e.g., Al outflow, sepiolite precipitation). Decreasing the maximum Cr from 0.125 to 0.025 increased sepiolite precipitation. Compared to simulation of only cation exchange, the inclusion of (kinetic) dissolution/precipitation reactions requires smaller time steps for the sequential non-iterative coupling method.

Heavy metal transport under atmospheric boundary conditions in a soil profile

The transport of solutes near the soil surface is influenced by near-surface water flow resulting from infiltration or precipitation and upward flow of water due to evapotranspiration. The newly coupled HYDRUS1D-PHREEQC model considers reactive transport during variably-saturated unsteady flow.

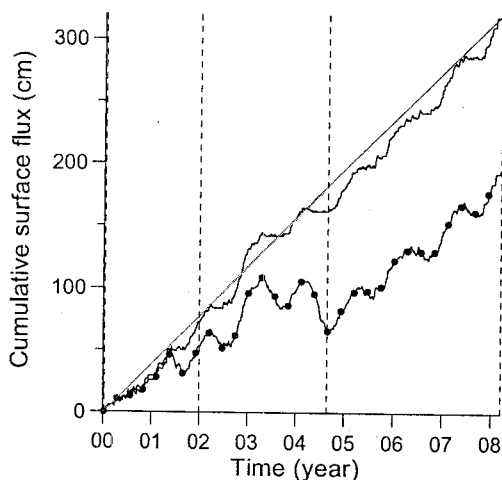


Figure 3. Atmospheric boundary conditions used for the heavy metal transport problem. Shown are the cumulative potential (black line with dots) and actual (black line) net surface water fluxes for the transient flow simulation, and the cumulative surface flux (gray line) for the steady-state simulation.

during dry periods. For example, the total concentration of Na increased significantly after a long dry period (at time 4.66 years). Because they are more closely held on the cation exchange complex, Ca and Cd show somewhat less pronounced accumulation. The effect of using atmospheric boundary conditions was relatively large: total concentrations were up to one order of magnitude higher than those calculated using steady-state boundary conditions. This result is important when, for example, modeling plant uptake of heavy metals or the degradation of organic contaminants.

CONCLUSIONS

The coupling of HYDRUS-1D simulating water flow and solute transport and PHREEQC for modeling a variety of biogeochemical reactions allows one to simulate a very broad range of interacting physical, chemical and biological processes affecting solute transport into and through soil. The combined code was tested successfully against an independent model (CRUNCH) for two benchmark problems.

Using the soil profile data from the first verification problem (but with a fixed CEC), the transport of Na, K, Ca, Mg, Cd, Zn, and Pb was simulated for a period of 8.2 year using meteorological data for the Kempen region (Belgium) for the period 1972 to 1981. Cumulative potential and actual net fluxes (precipitation minus potential or actual evaporation) across the soil surface are shown in Figure 3. The actual cumulative downward flux is higher than the potential flux since the sandy soil could not deliver enough water for evaporation during dry periods. In addition to the atmospheric boundary conditions, steady-state flow simulations were carried out with a constant surface flux of $0.107 \text{ cm day}^{-1}$.

Figure 4 shows distributions of the total concentrations C_T of Na, Ca, and Cd in the top 50 cm of the layered soil profile at four times. For the steady-state simulation, Ca and Cd concentrations decreased in the top 20 cm. Cd was almost completely leached from this layer due to aqueous complexation with Cl initially present in the soil solution. The use of atmospheric boundary conditions caused less leaching of elements from the top layer due to upward flow and transport

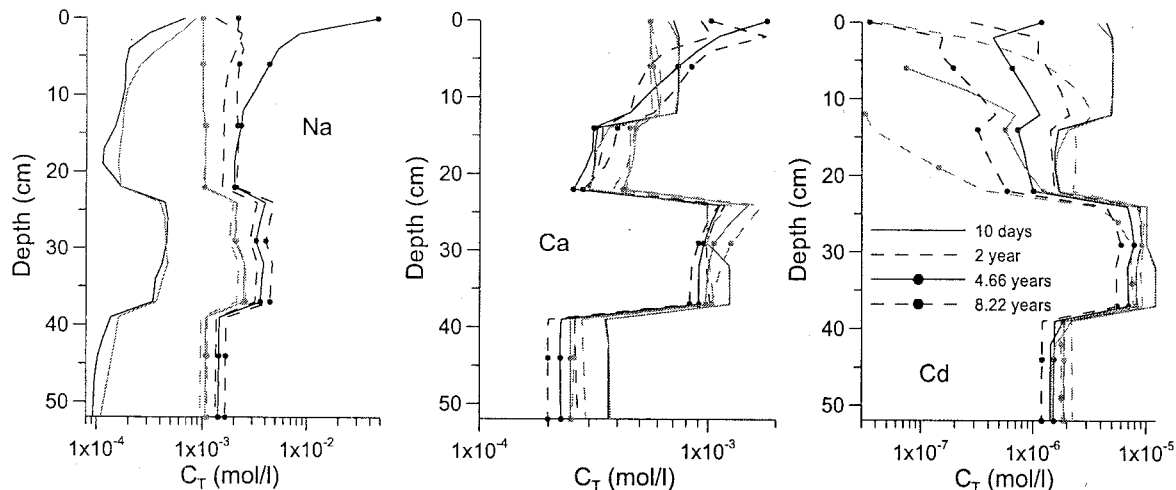


Figure 4. Distributions of the total concentration, C_T (mol/l), of Na, Ca, and Cd in the top 50 cm of a physically and chemically layered soil profile at four times during steady-state (gray lines) and atmospheric (precipitation/evaporation, black lines) flow conditions.

CRUNCH couples transport with geochemical reactions using either a global implicit approach (GIMRT) or a sequential non-iterative approach (SNIA). Results obtained with HYDRUS1D-PHREEQC were in excellent agreement with the CRUNCH simulations when SNIA was used. For small Courant numbers, the agreement with GIMRT was also satisfactory. A third example showed reduced leaching of cations and heavy metals from the top soil layer when transient precipitation–evaporation cycles were included in the model as compared to using steady-state flow conditions. This example demonstrated several features of the code for simulating solute transport subject to atmospheric boundary conditions.

Acknowledgment. This material is based on work supported in part by SAHRA (Sustainability of semi-Arid Hydrology and Riparian Areas) under the STC Program of the National Science Foundation, Agreement No. EAR-9876800.

REFERENCES

- Aagaard, P., and H. C. Helgeson, 1982. Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions, I. Theoretical considerations. *Am. J. Sci.*, 282:237-285.
- Adler, M., 2001. Interaction of claystone and hyperalkaline solutions at 30°C: A combined experimental and modeling study. Ph. Dissertation, Universität Bern, 120 p.
- Appelo, C.A.J., E. Verweij, and H. Schäfer, 1998. A hydrogeochemical transport model for an oxidation experiment with pyrite/calcite/exchangers/ organic matter containing sand. *Appl. Geochem.*, 13: 257-268.
- Parkhurst, D.L., and C.A.J. Appelo, 1999. User's guide to PHREEQC (version 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water Resources Investigations Report 99-4259, Denver, CO, USA, 312 pp.
- Šimůnek, J., M. Šejna, and M.Th. van Genuchten, 1998. The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media. Version 2.0, IGWMC-TPS-70, International Ground Water Modeling Center, Colorado School of Mines, Golden, CO, 202pp.
- Steeffel, C.I., 2000. New directions in hydrogeochemical transport modeling: Incorporating multiple kinetic and equilibrium reaction pathways. *Computational Methods in Water Resources XIII*, L.R. Bentley, J.F. Sykes, C.A. Brebbia, W.G. Gray, and G.F. Pinder (eds.), A.A. Balkema, Rotterdam, 331-338.
- Steeffel, C.I., and S.B. Yabusaki, 1996. OS3D/GIMRT; Software for multicomponent-multidimensional reactive transport; user manual and programmer's guide. PNL-11166, Pacific North West Laboratory, Richland, WA.