Multicomponent geochemical transport modeling using the HYDRUS computer software packages

J. Šimůnek[1], D. Jacques[2], M.Th. van Genuchten[3], and D. Mallants[2]
[1]*Department of Environmental Sciences, University of California Riverside, Riverside, CA 92521, USA, Jiri.Simunek@ucr.edu.*
[2]*Waste and Disposal Department, SCK•CEN, Boeretang 200, B-2400 Mol, Belgium.*
[3]*George E. Brown, Jr. Salinity Laboratory, USDA, ARS, 450 West Big Springs Road, Riverside, CA 92507, USA.*

1 INTRODUCTION

The subsurface fate and transport of agricultural and industrial contaminants, as well as many naturally occurring elements, is affected by a multitude of complex, interactive physical, chemical and biological processes. Water flow driven by capillary and gravitational forces, solute transport due to advection, dispersion and diffusion in the liquid and gaseous phases, as well as heat transport due to convection and conduction, are just a few of the physical processes active in the subsurface. Chemical processes include complexation reactions, cation exchange, precipitation-dissolution, sorption-desorption, volatilization, among other reactions. The transport and transformation of many contaminants is further mediated by subsurface aerobic or anaerobic bacteria. Bacteria catalyze redox reactions in which organic compounds act as the electron donor and inorganic substances (oxygen, nitrate, sulfate, or metal oxides) as the electron acceptor. Bacteria, by catalyzing such reactions, gain energy and organic carbon to produce new biomass. Simulating 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 summarize two recently developed coupled geochemical models that are both based on the widely used HYDRUS-1D software package (Šimůnek et al., 1998). One of these is restricted to the fate and transport of major ions, while the other model accounts for an unprecedented range of instantaneous and kinetic chemical and biological reactions.

2 GEOCHEMICAL MODELS

Šimůnek & Valocchi (2002) divided geochemical models into two major groups: those with specific chemistry, and more general models. Models with specific chemistry are limited in the number of species they can handle, while their application is generally restricted to problems having a prescribed chemical system. They are, however, much easier to use and computationally much more efficient than general models. Typical examples of models with specified chemistry are those simulating the transport of major ions, such as LEACHM (Wagenet and Hutson, 1987) and UNSATCHEM (Šimůnek & Suarez, 1994; Šimůnek et al., 1996), and various reclamation models (Šimůnek & Valocchi, 2002). Models with generalized chemistry include the DYNAMIX, HYDROGEOCHEM, MULTIFLO, FLOTRAN, and OS3D/GIMRT codes (see Šimůnek and Valocchi (2002) for a review of these codes), and HP1 (Jacques & Šimůnek, 2005). These models provide users with much more freedom in designing their particular chemical systems; they also permit a much broader range of applications.

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3 GEOCHEMICAL MODELS BASED ON HYDRUS-1D

3.1 HYDRUS-1D

HYDRUS-1D (Šimůnek et al., 1998) is a public domain computer software package (www.hydrus2d.com) that simulates the one-dimensional movement of water, heat, and multiple solutes in variably saturated media. The program numerically solves the Richards equation for saturated-unsaturated water flow and Fickian-based advection-dispersion equations for heat and solute transport. The flow equation incorporates a sink term to account for water uptake by plant roots. The heat transport equation considers conduction as well as advection with flowing water. The solute transport equations assume advective-dispersive transport in the liquid phase, and diffusion in the gaseous phase. The transport equations also include provisions for nonlinear and/or nonequilibrium reactions between the solid and liquid phases, linear equilibrium reactions between the liquid and gaseous phases, zero-order production, and two first-order degradation reactions: one which is independent of other solutes, and one which provides the coupling between solutes involved in the sequential first-order decay reactions. The software package may be used to analyze water and solute movement in unsaturated, partially saturated, or fully saturated porous media. Root growth is simulated by means of a logistic growth function. Water and salinity stress response functions can also be considered.

HYDRUS-1D uses a Microsoft Windows based Graphics User Interface (GUI) to manage the input data required to run the program, as well as for nodal discretization and editing, parameter allocation, problem execution, and visualization of results. All spatially distributed parameters, such as those for various soil horizons, the root water uptake distribution, and the initial conditions for water, heat and solute movement, are specified in a graphical environment. HYDRUS-1D offers graphs of the distributions of the pressure head, water content, water and solute fluxes, root water uptake, temperature and solute concentrations in the soil profile at pre-selected times. A small catalog of soil hydraulic properties, as well as pedotransfer functions based on neural networks, are included in the program.

3.2 *Specific chemistry model*

As an alternative to the solute transport module described above, we recently implemented a major ion chemistry module based on the UNSATCHEM model (Šimůnek & Suarez, 1994, 1997; Šimůnek et al., 1996). This module considers the transport of major ions and carbon dioxide in soils. CO_2 transport is assumed to be governed by diffusion in both the liquid and gas phases, and by advection in the liquid phase. The major variables of the chemical system are Ca, Mg, Na, K, SO_4, Cl, NO_3, H_4SiO_4, alkalinity, and CO_2 (Table 1). The model accounts for equilibrium chemical reactions between these components such as complexation, cation exchange and precipitation-dissolution. For the precipitation-dissolution of calcite and dissolution of dolomite, either equilibrium or multicomponent kinetic expressions can be used, which include both forward and backward reactions. Other precipitation-dissolution reactions considered involve gypsum, hydromagnesite, nesquehonite, and sepiolite. Since the ionic strength of soil solutions can vary considerably in time and space and often reaches high values, both the modified Debye-Hückel and Pitzer expressions were incorporated into the model, thus providing options for calculating single ion activities. The new UNSATCHEM module of HYDRUS-1D enables quantitative predictions for processes that involve major ions, such as simulations of the effects of salinity on plant growth and the amount of water and amendment required to reclaim soil profiles to desired levels of salinity and ESP (exchangeable sodium percentage).

Table 1 Chemical species considered by the major ion 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	$CaCO_3$, $CaSO_4 \cdot 2H_2O$, $MgCO_3 \cdot 3H_2O$, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$, $Mg_2Si_3O_{7.5}(OH) \cdot 3H_2O$, $CaMg(CO_3)_2$
4	Sorbed (exchangeable) species	4	Ca, Mg, Na, K
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, $H_3SiO_4^{-}$, $H_2SiO_4^{2-}$

3.3 *General chemistry model*

HYDRUS-1D was recently coupled also with the PHREEQC geochemical code (Parkhurst & Appelo, 1999) to create a new comprehensive simulation tool, HP1 (HYDRUS1D-PHREEQC) (Jacques et al., 2003; Jacques & Šimůnek, 2005). This new code contains modules simulating (1) transient water flow in variably-saturated media, (2) the transport of multiple components, and (3) mixed equilibrium/kinetic geochemical reactions. HP1 is a significant expansion of the individual HYDRUS-1D and PHREEQC programs by preserving most of their original features and capabilities. The code still uses the Richards equation for simulating variably-saturated water flow and advection-dispersion type equations for heat and solute transport. But the program can now simulate also a broad range of low-temperature biogeochemical reactions in water, the vadose zone and ground water systems, including interactions with minerals, gases, exchangers, and sorption surfaces, based on thermodynamic equilibrium, kinetics, or mixed equilibrium-kinetic reactions.

Jacques et al. (2003) and Jacques & Šimůnek (2005) demonstrated the versatility of HP1 on various examples involving a) transport of heavy metals (Zn^{2+}, Pb^{2+}, and Cd^{2+}) subject to multiple cation exchange, b) transport with mineral dissolution of amorphous SiO_2 and gibbsite ($Al(OH)_3$), c) heavy metal transport in a medium with a pH-dependent cation exchange complex, d) infiltration of a hyperalkaline solution in a clay sample (this example considers kinetic precipitation-dissolution of kaolinite, illite, quartz, calcite, dolomite, gypsum, hydrotalcite, and sepiolite), and e) 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.

As an example application of HP1, Figure 1 shows calculated effluent concentrations of heavy metals (Zn^{2+}, Pb^{2+}, and Cd^{2+}) leached from a 10-cm soil column. Heavy metals initially present in the soil column are leached from the exchange complex by major ions (Ca^{2+}, Mg^{2+}, and Al^{3+}). Details are given by Jacques & Šimůnek (2005).

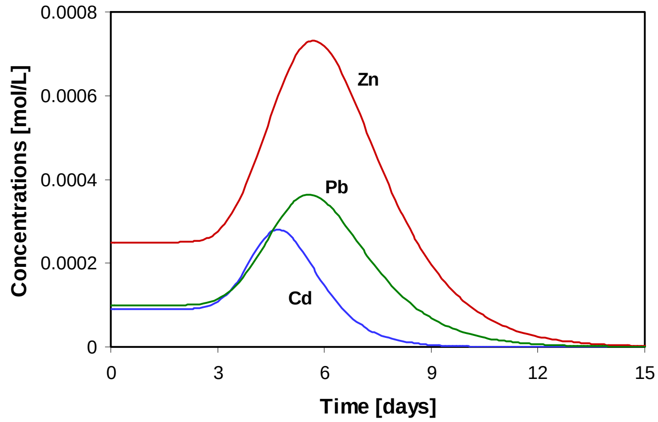

Figure 1. Zn, Pb, and Cd concentrations in the effluent of a 10-cm soil long column.

4 SUMMARY AND CONCLUSIONS

We presented two new comprehensive simulation tools based on the HYDRUS-1D software package. While the UNSATCHEM module (directly incorporated into HYDRUS-1D) is restricted to a specific chemical system involving the transport and reactions of major ions (thus making the program relatively easy to use), HP1 (HYDRUS1D-PHREEQC) accounts for an unprecedented range of instantaneous and kinetic chemical and biological reactions, including complexation, cation exchange, surface complexation, precipitation-dissolution, and/or redox reactions (thus requiring users to be more familiar with the chemistry involved).

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