

MULTICOMPONENT GEOCHEMICAL TRANSPORT
MODELING USING HYDRUS-1D AND HP1¹

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ABSTRACT: The transport of reactive contaminants in the subsurface is generally affected by a large number of nonlinear and often interactive physical, chemical, and biological processes. Simulating these processes requires a comprehensive reactive transport code that couples the physical processes of water flow and advective-dispersive transport with a range of biogeochemical processes. Two recently developed coupled geochemical models that are both based on the HYDRUS-1D software package for variably saturated flow and transport are summarized in this paper. One model resulted from coupling HYDRUS-1D with the UNSATCHEM module. While restricted to major ion chemistry, this program enables quantitative predictions of such problems as analyzing the effects of salinity on plant growth and the amount of water and amendments required to reclaim salt-affected soil profiles. The second model, HP1, resulted from coupling HYDRUS-1D with the PHREEQC biogeochemical code. The latter program accounts for a wide range of instantaneous or kinetic chemical and biological reactions, including complexation, cation exchange, surface complexation, precipitation dissolution and/or redox reactions. The versatility of HP1 is illustrated in this paper by means of two examples: the leaching of toxic trace elements and the transport of the explosive TNT and its degradation products.

(KEY TERMS: vadose zone; transport and fate; transport models; heavy metals; multicomponent geochemical transport; reclamation models.)

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INTRODUCTION

A multitude of interactive physical, chemical, and biological processes generally affects the fate and transport of reactive agricultural and industrial contaminants, as well as many naturally occurring elements, in the subsurface. Physical processes in the subsurface may include capillary and gravitational forces that cause transient water flow; advection, dispersion and diffusion in the liquid and gaseous phases that lead to solute transport; and convection and conduction that result in heat transport. The soil solution is always a mixture of many ions that may be involved in mutually dependent chemical processes such as complexation reactions, cation exchange, precipitation-dissolution, sorption-desorption, volatilization, redox reactions, and degradation (Šimunek and Valocchi, 2002; Appelo and Postma, 2005). The transport and transformation of many contaminants is further mediated by subsurface aerobic or anaerobic bacteria. Bacteria catalyze redox reactions in which organic compounds (e.g., hydrocarbons) act as the electron donor and inorganic substances (oxygen, nitrate, sulfate, or metal oxides) as the electron acceptor. By catalyzing such reactions, bacteria gain energy and organic carbon to produce new biomass. The transport of bacteria is generally more complex than that of other solutes in that they are affected by such additional processes as filtration, straining, sedimentation, adsorption, and desorption, growth, and inactivation (e.g., Bradford *et al.*, 2003; van Genuchten and Šimunek, 2004). These and related processes can be

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simulated using integrated reactive transport codes that couple the physical processes of water flow and advective-dispersive solute transport with a range of biogeochemical processes.

In this paper two recently developed coupled geochemical models are summarized that are both based on the HYDRUS-1D software package for simulating variably saturated flow and transport (Šimůnek *et al.*, 1998). The first program, which resulted from coupling HYDRUS-1D with the UNSATCHEM module (Šimůnek *et al.*, 1996), is restricted to major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , and HCO_3^- , and their complexes). This program enables quantitative predictions of such problems as analyzing the effects of salinity on plant growth, water and salinity management practices and irrigation techniques under arid and semiarid conditions, evaluation of water suitability for irrigation, and estimating the amount of water and amendments required to reclaim salt-affected soil profiles. The other program (HP1) resulted from coupling HYDRUS-1D with the PHREEQC geochemical code (Parkhurst and Appelo, 1999). This program accounts for a wide range of instantaneous and kinetic chemical and biological reactions. Several examples will be given to demonstrate the utility of both programs.

COUPLED GEOCHEMICAL MODELS

As summarized by Šimůnek and Valocchi (2002), geochemical transport models can be divided into two major groups: those with specific chemistry and more general models. Models with specific chemistry are generally restricted to certain prescribed chemical systems and thus are usually constrained to very specific applications. However, they are often much easier to use and computationally much more efficient than general models. Models simulating the transport of major ions, such as LEACHM (Wagenet and Hutson, 1987) and UNSATCHEM (Šimůnek and Suarez, 1994; Šimůnek *et al.*, 1996), and various reclamation models (Šimůnek and Valocchi, 2002) are typical examples of models with specific chemistry. These models typically consider the transport of major ions and their mutual reactions such as complexation, cation exchange, and precipitation/dissolution. Models simulating carbon and nitrogen cycles are also becoming a standard feature of many environmental models, for example in DAISY (Hansen *et al.*, 1990), LEACHM (Hutson and Wagenet, 1992), RZWQM (Ahuja and Hebron, 1992), COUP (Jansson and Karlberg, 2001), and HYDRUS-2D coupled with CW2D (Langergraber and Šimůnek, 2005). These models typically distribute organic matter, carbon,

and organic and mineral nitrogen over multiple computational pools while allowing organic matter to be decomposed by multiple microbial biomass populations. They can account for most of the major reaction pathways, such as interpool transfer of carbon and nitrogen, nitrification (ammonium to nitrate-N), denitrification (leading to the production of N_2 and N_2O), volatilization losses of ammonia (NH_3), and microbial biomass growth and death.

On the other hand, models with generalized chemistry provide users with much more freedom in designing particular chemical systems and thus also permit a much broader range of applications. Users can either select species and reactions from large geochemical databases or define their own species with particular chemical properties and reactions. These models generally invoke a variety of sequential iterative or noniterative operator splitting approaches in which transport and chemistry are numerically solved in separate steps. Examples of models with generalized chemistry have been recently reviewed by Šimůnek and Valocchi (2002) and Jacques *et al.* (2006). Most codes with general geochemistry are limited to solute transport and biogeochemical reactions, while water flow paths have to be calculated outside of the reactive transport code (e.g., PHREEQC, Parkhurst and Appelo, 1999; CRUNCH, Steefel, 2000; PHAST, Parkhurst *et al.*, 2004). Only a few models allow the velocity field to be calculated internally. Several codes for transient unsaturated flow have also been coupled to general biogeochemistry models. These include, for example, 3DHYDROGEOCHEM (Yeh and Cheng, 1999) and HP1 (Jacques and Šimůnek, 2005).

The HYDRUS-1D (Version 3.0) (Šimůnek *et al.*, 2005) and HP1 models (Jacques and Šimůnek, 2005) that represent typical examples of models with specific and generalized chemistry, respectively, are discussed below.

Overview of HYDRUS-1D

HYDRUS-1D (Šimůnek *et al.*, 2005) 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 uses finite elements to numerically solve the Richards equation for saturated unsaturated water flow and Fickian-based advection-dispersion equations for both heat and solute transport. The flow equation includes a sink term to account for water uptake by plant roots as a function of both water and salinity stress. 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 that is independent of other solutes and one that provides the coupling between solutes involved in the sequential first-order decay reactions. The program allows analysis of flow and transport in both unsaturated, partially saturated, or fully saturated media. The flow region itself may consist of nonuniform (layered) soils. The unsaturated soil hydraulic properties (the constitutive relationships) are described using Brooks and Corey (1964), van Genuchten (1980), Durner (1994), and Kosugi (1996) type analytical functions; Durner (1994) uses modified van Genuchten type functions that permit a better description of the hydraulic properties near saturation. The software optionally also considers hysteresis by assuming that drying scanning curves are scaled from the main drying curve and wetting scanning curves from the main wetting curve.

Root growth in HYDRUS-1D is simulated by means of a logistic growth function. Water and salinity stress-response functions also can be considered. Physical nonequilibrium solute transport can be accounted for by assuming a two-region, dual-porosity type formulation that partitions the liquid phase into separate mobile and immobile regions. HYDRUS-1D was recently modified to also allow simulations of the transport of viruses, colloids, and bacteria (Schijven and Šimůnek, 2002; Bradford *et al.*, 2003). In addition, HYDRUS-1D implements a Marquardt-Levenberg type parameter estimation technique (Marquardt, 1963; Šimůnek and Hopmans, 2002) for inverse estimation of soil hydraulic (Hopmans *et al.*, 2002) and/or solute transport and reaction (Šimůnek *et al.*, 2002) parameters from measured transient or steady state flow and/or transport data. The main new features of the current version 3.0, as compared to version 2.0, are new analytical models for the soil hydraulic properties (i.e., the Kosugi and Durner analytical models), provisions for compensated root water uptake, dual porosity features for water flow, attachment/detachment models for solute transport to allow simulations of virus, colloid, and bacteria transport, and modules for carbon dioxide dynamics and for major ion chemistry.

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. The program 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. Also included are a small catalog of unsaturated soil hydraulic properties (Carsel and Parish, 1988) and a set of pedotransfer functions based on neural networks (Schaap *et al.*, 2001).

The general formulation of the transport equations in the HYDRUS codes allows one to simulate not only non-adsorbing and linearly or nonlinearly sorbing chemicals but also a variety of other contaminants such as viruses (Schijven and Šimůnek, 2002), colloids (Bradford *et al.*, 2003), and cadmium (Seuntjens *et al.*, 2001) or chemicals involved in the sequential biodegradation reactions such as chlorinated aliphatic hydrocarbons (Schaerlaekens *et al.*, 1999; Casey and Šimůnek, 2001) or hormones (Casey *et al.*, 2003).

Specific (Major Ion) Chemistry Module of HYDRUS-1D

The solute transport module of HYDRUS-1D as described above is limited to single ions or ions subject to relatively simple first-order consecutive decay reactions (e.g., nitrification-denitrification chains, or radionuclide decay chains). As an alternative to this approach, we recently implemented into HYDRUS-1D a major ion chemistry module based on the UNSATCHEM model (Šimůnek and Suarez, 1994, 1997; Šimůnek *et al.*, 1996, 2005). This module considers the transport of major ions and carbon dioxide in soils. CO₂ transport is assumed to be governed by diffusion in both the liquid and gas phases, by advection in the liquid phase, and by respiration by both soil microorganisms and plant roots.

The major variables of the UNSATCHEM chemical system are Ca, Mg, Na, K, SO₄, Cl, NO₃, H₄SiO₄, alkalinity, and CO₂ (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 (CaCO₃) and the dissolution of dolomite (MgCO₃·3H₂O), either equilibrium or multicomponent kinetic expressions can be used, including both forward and backward reactions. Other precipitation-dissolution reactions considered involve gypsum (CaSO₄·2H₂O), hydromagnesite (Mg₅(CO₃)₄(OH)₂·4H₂O), nesquehonite (MgCO₃·3H₂O), and sepiolite (Mg₂Si₃O_{7.5}(OH)·3H₂O). Since the ionic strength of soil solutions can vary considerably in time and space and often reach high

TABLE 1. Chemical Species Included in the Major Ion Module of HYDRUS-1D.

Aqueous Components	7	Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , Cl^- , NO_3^-
Complexed Species	10	CaCO_3^0 , CaHCO_3^+ , CaSO_4^0 , MgCO_3^0 , MgHCO_3^+ , MgSO_4^0 , NaCO_3^- , NaHCO_3^0 , NaSO_4^- , KSO_4^-
Precipitated Species	6	CaCO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, $\text{Mg}_2\text{Si}_3\text{O}_7.5(\text{OH}) \cdot 3\text{H}_2\text{O}$, $\text{CaMg}(\text{CO}_3)_2$
Sorbed (exchangeable) Species	4	Ca, Mg, Na, K
CO_2 - H_2O Species	7	PCO_2 , H_2CO_3^* , CO_3^{2-} , HCO_3^- , H^+ , OH^- , H_2O
Silica Species	3	H_4SiO_4 , H_3SiO_4^- , $\text{H}_2\text{SiO}_4^{2-}$

values, both the modified Debye-Hückel (Truesdell and Jones, 1974) and Pitzer (Pitzer, 1979) expressions were incorporated into the model, thus providing options for calculating single-ion activities. This module also considers the effects of solution composition on the unsaturated soil hydraulic properties. The new UNSATCHEM module of HYDRUS-1D enables quantitative predictions of processes involving major ions, such as simulations of the effects of salinity on root water uptake and plant growth, evaluation of alternative irrigation, salinity and crop management practices, evaluation of water suitability for irrigation, and estimation of the amount of water and amendment required to reclaim soil profiles to desired levels of salinity and exchangeable sodium percentage (ESP). A recent application of HYDRUS-1D and its major ion chemistry module is given by Gonçalves *et al.* (2006), who simulated solute transport in three lysimeters irrigated with different-quality waters over a time period of three years. HYDRUS-1D successfully described field measurements not only of the overall salinity but also of individual soluble cations as well as sodium adsorption ratio (SAR) and ESP (Gonçalves *et al.*, 2006).

A typical application of the above UNSATCHEM major ion chemistry module within HYDRUS-1D is sodic soil reclamation involving the removal of excessive salts from the soil profile and replacement of exchangeable Na^+ with Ca^{2+} . This problem is relatively complicated in that one must simulate not only variably saturated water flow and solute transport but also the dissolution of solid phases (i.e., of reclamation amendments such as gypsum or calcite), cation exchange (replacement of Na^+ with Ca^{2+}), complexation reactions, the effects of solution composition on hydraulic conductivities and infiltration rates, and the effects of elevated CO_2 concentrations on pH and hence on calcite dissolution (Šimůnek and Suarez, 1997). We briefly summarize here results of a hypothetical sodic soil reclamation study by Šimůnek and Suarez (1997), who considered six reclamation strategies. In the first two cases, (A) high quality (i.e., low ion concentration) and (B) gypsum saturated waters

were applied to the soil without additional amendments. In the third example, (C) high quality water was applied to a soil profile in which gypsum was incorporated in the top 20 cm. In three other cases, (D) high quality water or water having one of two different acid concentrations at (E) pH = 2.05 and (F) at pH = 1.09 were applied to the surface of a calcareous soil. The solution composition of water initially present in the soil profile was assumed to be that of a typical highly sodic soil system. The cation exchange capacity was set at 200 mmol_c/kg and the ESP at 60 (Ca = 40.0, Mg = 40.0, Na = 120.0 mmol_c/kg). The solution composition of four irrigation waters used for the reclamation process is given in Table 2. Model-predicted CO_2 concentrations were used for the last three cases, where CO_2 has an important effect on calcite dissolution. All calculations considered hydraulic conductivity reductions due to changes in the solution composition. The example assumes that the soil surface was flooded with water, with the water kept at a constant level of 1 cm above the soil surface.

Figure 1 shows calculated sodium adsorption ratio, SAR [=Na/((Ca+Mg)/2)^{0.5}], profiles for all six reclamation strategies. The various scenarios were evaluated in terms of the time required for reclamation to be completed and the amount of water needed for this. Times to full profile saturation (saturation equal to porosity) for the six strategies above were calculated to be 358, 15.3, 2.0, 10, 6.4, and 3.2 days, respectively. Times to profile reclamation were 86,870, 195.6, 116.5, 91, 64, and 15.5 days, respectively, while the amounts of infiltrated water needed for reclamation were 7,230, 559, 470, 600, 485, and 197 cm, respectively (Šimůnek and Suarez, 1997). The first strategy was included only as a reference to compare with other scenarios, mainly to emphasize the effects of gypsum and calcite dissolution on reclamation. This strategy is clearly inappropriate for sodic soil reclamation, since high quality water does not have a sufficient supply of calcium to replace the exchangeable sodium and as such can lead to soil dispersion and subsequent reductions in the hydraulic conductivity.

TABLE 2. Solution Composition of Waters Used in the Reclamation Example (in $\text{mmol}_c\text{L}^{-3}$).

Water	Ca_T	Mg_T	Na_T	Cl_T	SO_4T	Alkalinity	Used in Scenario
High Quality	1.5	0.5	2.0	1.0	2.5	0.5	A,C,D
Gypsum Saturated	32.0	0.5	2.0	1.0	33.0	0.5	B
Acid Water I	1.5	0.5	2.0	3.0	11.0	-10.0	E
Acid Water II	1.5	0.5	2.0	93.0	11.0	-100.0	F
Initially Present in the Soil	0.2	0.2	4.8	4.8	0.0	0.4	A,B,C,D,E,F

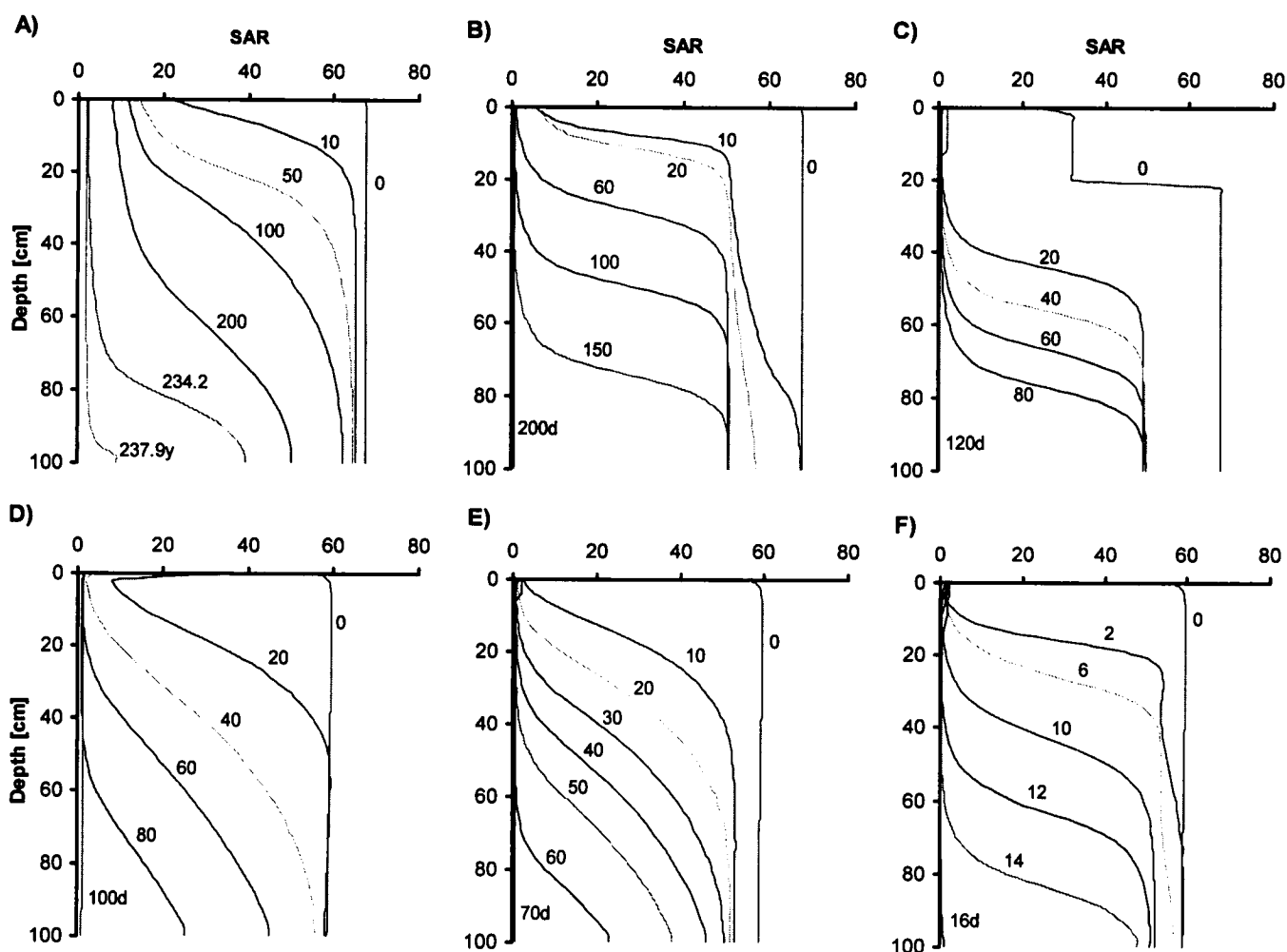


Figure 1. Sodium Adsorption Profiles for Six Reclamation Strategies. (A) Irrigation with high quality water and no amendments; (B) Irrigation with gypsum saturated water; (C) Irrigation with high quality water and gypsum incorporated in the top 20 cm; (D) Irrigation with high quality water and with calcite present in the entire soil profile; (E) Irrigation with acid water at pH 2.05 and with calcite in the entire soil profile; and (F) Irrigation with acid water at pH = 1.09 and with calcite in the entire soil profile (after Šimůnek and Suarez, 1997).

Since sodic soil reclamation is a relatively complex problem, only models that quantitatively integrate all of the major processes involved should be used, rather

than resorting to highly simplified models based on single-ion or decay chain transport (Šimůnek and Valocchi, 2002).

The HP1 General Chemistry Model

HYDRUS-1D was recently coupled also with the PHREEQC geochemical code (Parkhurst and Appelo, 1999) to create a new comprehensive simulation tool, HP1 (acronym for HYDRUS1D-PHREEQC) (Jacques *et al.*, 2003; Jacques and Šimůnek, 2005; Šimůnek *et al.*, 2005). This new code contains modules simulating transient water flow in variably saturated media, the transport of multiple components, mixed equilibrium/kinetic biogeochemical reactions, and heat transport. HP1 becomes 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. However, the loosely coupled program can now simulate also a broad range of low-temperature biogeochemical reactions in water, the vadose zone and in ground water systems, including interactions with minerals, gases, exchangers, and sorption surfaces based on thermodynamic equilibrium, kinetic, or mixed equilibrium-kinetic reactions. HP1 uses the operator splitting approach with no iterations during one time step (noniterative sequential approach). Jacques *et al.* (2006) evaluated the accuracy of the operator splitting approach for a kinetic reaction network (i.e., sequential and parallel kinetic degradation reactions) by comparing HP1 with an analytical solution for trichloroethylene (TCE) degradation and for mixed equilibrium and kinetic reactions involving different flow conditions (steady state and transient). HP1 is available on request from www.sckcen.be/hp1. The current version of HP1 is limited to one-dimensional flow and transport problems and does not consider oxidation reduction reactions, surface complexation, and diffusion of components in the gas phase. These reactions will be available in upcoming versions currently under development (Jacques *et al.*, 2005b).

Jacques *et al.* (2003, 2005a) and Jacques and Šimůnek (2005) demonstrated the versatility of HP1 on several examples such as the transport of heavy metals (Zn^{2+} , Pb^{2+} , and Cd^{2+}) subject to multiple cation exchange reactions; transport with mineral dissolution of amorphous SiO_2 and gibbsite, $Al(OH)_3$; heavy metal transport in a medium with a pH dependent cation exchange complex; 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); 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;

cadmium leaching in acid sandy soils; radionuclide transport; and long-term uranium migration in agricultural field soils following mineral P-fertilization. The first example is briefly discussed below, together with a new application that involves the fate and sub-surface transport of explosives.

Leaching of Heavy Metals From a Soil Column. As a first example application of HP1, Figure 2 shows calculated effluent concentrations of major ions (Ca^{2+} , Na^+ , Al^{3+} , and Cl^-) and heavy metals (Zn^{2+} , Pb^{2+} , and Cd^{2+}) leached from a soil column 8 cm long having an initial solution as defined in Table 3 and with its ion exchange complex in equilibrium with this solution. Heavy metals initially on the exchange complex are being replaced during the leaching process by major ions (Ca^{2+} , Mg^{2+} , and Al^{3+}). Ca rich water with a chemical composition as given in Table 3 was applied to the top of the column at a steady flow rate of 2 cm day⁻¹. The longitudinal dispersivity was assumed to be 0.2 cm.

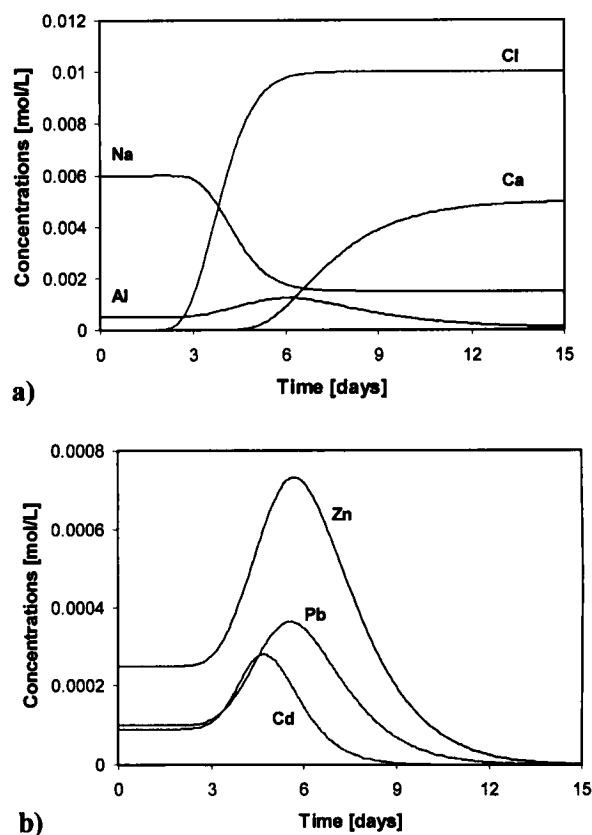


Figure 2. Concentrations of (a) Major Ions and (b) Heavy Metals (Zn, Pb, and Cd) in the Effluent From an 8 cm Long Soil Column.

The example considered the transport of ten ions (Al, Br, Ca, Cd, Cl, K, Mg, Na, Pb, Zn) during a 15-day period. Removal of Cd, Pb and Zn from the solid

TABLE 3. Chemical Components (mmol/L) and Species Considered, and Elemental Compositions of Initial and Boundary Solutions Used in the Column Simulation (X refers to ion exchanger).

Components	Species	Solutions	
		Boundary	Initial
Al	Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3^0$, $\text{Al}(\text{OH})_4^-$	0.1	0.5
Br	Br^-	3.7	11.9
Cl	Cl^- (and Cd, Pb, and Zn-species, see below)	10	0
Ca	Ca^{2+} , $\text{Ca}(\text{OH})^+$	5	0
K	K^+ , KOH^0	0	2
Na	Na^+ , NaOH^0	0	6
Mg	Mg^{2+} , $\text{Mg}(\text{OH})^+$	1	0.75
Cd	Cd^{2+} , $\text{Cd}(\text{OH})^+$, $\text{Cd}(\text{OH})_2^0$, $\text{Cd}(\text{OH})_3^-$, $\text{Cd}(\text{OH})_4^{2-}$, CdCl^+ , CdCl_2 , CdCl_3^-	0	0.9
Pb	Pb^{2+} , $\text{Pb}(\text{OH})^+$, $\text{Pb}(\text{OH})_2^0$, $\text{Pb}(\text{OH})_3^-$, $\text{Pb}(\text{OH})_4^{2-}$, PbCl^+ , PbCl_2^0 , PbCl_3^- , PbCl_4^{2-}	0	0.1
Zn	Zn^{2+} , $\text{Zn}(\text{OH})^+$, $\text{Zn}(\text{OH})_2^0$, $\text{Zn}(\text{OH})_3^-$, $\text{Zn}(\text{OH})_4^{2-}$, ZnCl^+ , ZnCl_2^0 , ZnCl_3^- , ZnCl_4^{2-}	0	0.25
X	AlX_3 , AlOHX_2 , CaX_2 , CdX_2 , KX , NaX , MgX_2 , PbX_2 , ZnX_2 (mmol)	NA	11

phase was calculated to occur by ion exchange with mostly Ca and to a lesser degree with Mg. The 8 cm-long soil column for the numerical calculations was discretized into 40 elements of 0.2 cm each. More details about numerical stability and its dependence on the selected temporal and spatial discretization, the cation exchange complex, and the solution precision are given by Jacques and Šimůnek (2005).

Transport of TNT and Its Daughter Products.

The second example deals with the fate and transport of explosive species. Concern is increasing about the presence of explosives and energetics in the subsurface environment. Such chemicals are the result of the manufacture, distribution, testing and/or unsafe disposal of ammunition. Contamination of soil and water resources with residues of major explosives and energetics now constitutes a widespread environmental problem. These include TNT (2,4,6-trinitrotoluene); RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine); HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine); picric acid; tetryl, hexyl, nitroglycerin; and PETN; as well as their principal transformation products (notably 2ADNT, 4ADNT, 2,4DANT, 2,6DANT, 1,3,5TNB, 1,3DNB, NB, and 3,5DNA) and some of their manufacturing impurities (2,4DNT and 2,6DNT) (Gorontzy *et al.*, 1994; Brannon and Pennington, 2002). Many of these compounds are known or suspected to be potentially toxic, mutagenic, or carcinogenic. The chemicals have been found not only at ammunition production and handling facilities in the United States and worldwide but also at many disposal sites and army testing, training, and firing ranges,

among other places (Pennington *et al.*, 2001; Brannon and Pennington, 2002). They often leach through the vadose zone into ground water and thus threaten underlying or downgradient water resources. The cost to complete the current U.S. Department of Defense (DoD) cleanup program using traditional approaches is estimated to be more than \$35 billion (Pennington *et al.*, 1999a).

Previous efforts to model the transport of major explosives have been based mostly on either Modflow (Harbaugh *et al.*, 2000) combined with MT3D (Zheng and Wang, 1999) for ground water systems or FEMWATER (Yeh *et al.*, 1992) for vadose zone type investigations (Pennington *et al.*, 1999b). Neither of these codes at present accounts for all of the processes known or hypothesized to affect the fate and subsurface transport of explosives and their metabolites, such as nonlinear and kinetic dissolution and sorption, simultaneous transport of multiple metabolites, simultaneous transport in both the liquid and vapor phase, and the temperature dependence of transport and reaction parameters. Most or all of these processes can be simulated with HP1 and other biogeochemical models such as 3DHYDROGEOCHEM or CRUNCH – notably the transport of the major explosives themselves (the parent products) such as TNT, RDX, or HMX but also the various metabolites (the daughter products) such as 2ADNT, 2,4DANT, 1,3,5TNB as they are being created sequentially by degradation of the parent compounds. HP1 further allows the parent and daughter compounds to have different mobilities in the subsurface as dictated by their specific dissolution, sorption and transport

properties. In its most general case, the model permits contaminants to reside in all three phases, i.e., the liquid, solid (precipitated and sorbed), and gaseous phases. HP1 allows for multiple degradation pathways that involve both diverging and converging branches. Since users of HP1 can define any kinetic reaction through its Basic interpreter, there is virtually no limitation on the complexity of processes calculated. An example of an initially diverging and then converging branch is TNT degradation, which may proceed along two branches before reaching the compound 2,4,6-trinitrotoulene (TAT) by reductive biotransformation (Figure 3).

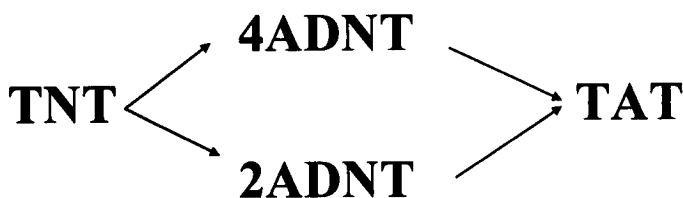


Figure 3. Degradation Pathway of TNT (2,4,6-trinitrotoluene) Through Two Degradation Products 2ADNT (2-amino-4,6-dinitrotoluene) and 4ADNT (4-amino-2,6-dinitrotoluene) to TAT (2,4,6-trinitrotoulene).

The example here considers the fate and transport of four explosive species in a 100 cm deep fully saturated soil profile leached for 10 days at a water flux rate of 1 cm/h and using a longitudinal dispersivity equal to 5 cm. TNT, the parent product, was assumed to be initially present in the top 5 cm of the soil at a concentration of 1 mg/kg (6.61e-6 mol). The kinetic dissolution rate (mol/h) of TNT is given as

$$r = Ak \left(1 - \frac{[\text{TNT}]}{K} \right) \tag{1}$$

where A is the reactive surface of TNT (assumed to be 1 cm² and kept constant during the simulation), k is the dissolution rate (equal to 1.8e-5 mol/cm²/h), and K is the equilibrium constant of TNT dissolution, $\log(K) = -5.356$. When dissolved, TNT was assumed to degrade at a rate of 0.01 1/h to form the daughter products 2ADNT (2-amino-4,6-dinitrotoluene) (66.7 percent) and 4ADNT (4-amino-2,6-dinitrotoluene) (33.3 percent), which further degrade at rates of 0.006 and 0.04 1/h, respectively, to produce the same final daughter product TAT (Pennington *et al.*, 1999b). The distribution coefficients, K_D , for linear sorption were assumed to be equal to 3, 5, 6, and 0 L/kg for TNT, 2ADNT, 4ADNT, and TAT, respectively (Pennington *et al.*, 1999b). Figure 4 shows calculated breakthrough curves at 50 and 100 cm depths, and Figure 5 shows

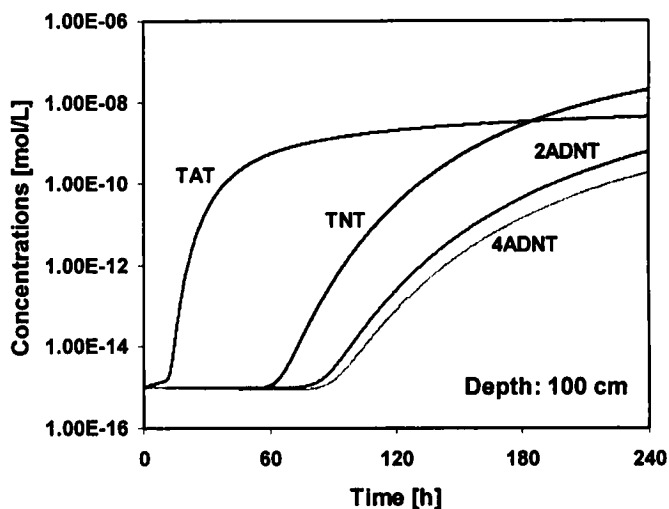
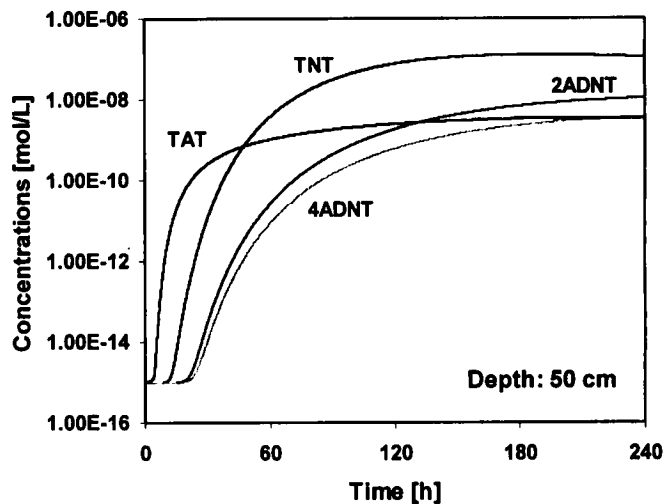


Figure 4. Breakthrough Curves at Depths of 50 and 100 cm for TNT, 2ADNT, 4ADNT, and TAT.

simulated concentration distributions versus depth. Although TAT is the last daughter product, it arrived at the 50 and 100 cm depths before the other species as a result of having the smallest distribution coefficient and due to the relatively short half-life of 4ADNT ($T_{1/2} = 17.3$ h) (Figure 4). Because of the much longer half-life of 2ADNT ($T_{1/2} = 115.5$ h), most of the observed TAT present at early times is due to degradation of 4ADNT. And while concentrations of TNT were initially highest (e.g., after 2 d in Figure 5) and then decreased due to degradation, concentrations of all daughter species (2ADNT, 4ADNT, and TAT) always increased during the 10-day simulation. Because of less sorption, TAT moved fastest through the soil profile, followed by TNT, and then 2ADNT and 4ADNT at very similar velocities. This example demonstrates that ground water may be more vulnerable to leaching of TNT daughter products (notably

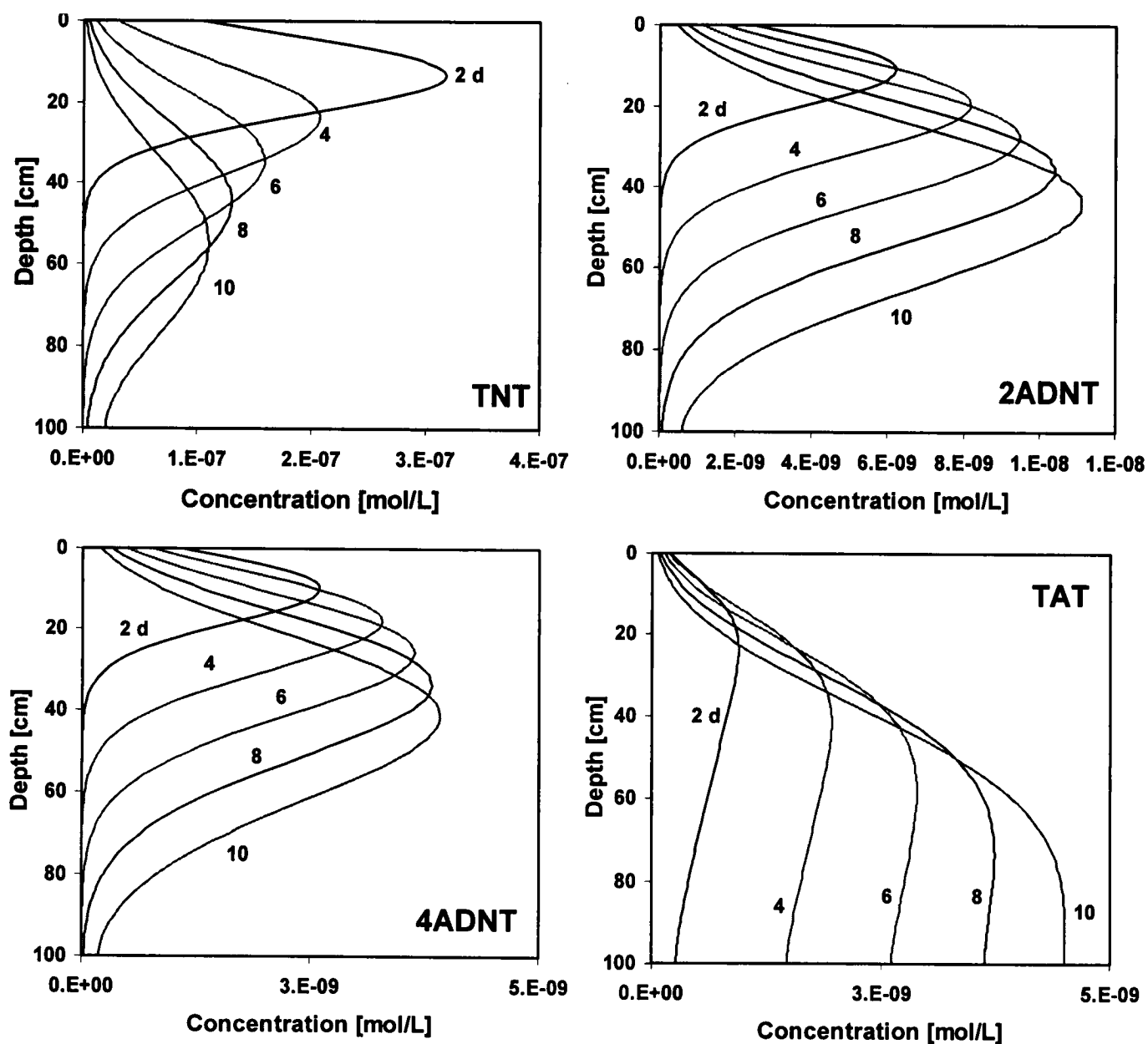


Figure 5. Concentration Profiles for TNT, 2ADNT, 4ADNT, and TAT (0 to 10 days)

TAT) than of the parent compound itself and that sensors detecting daughter products may provide an early warning of possible TNT leaching.

SUMMARY AND CONCLUSIONS

Two new comprehensive simulation tools based on the HYDRUS-1D software package were presented in this paper. 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, but rather restrictive in terms of its range of applications – HP1 (HYDRUS1D-PHREEQC) accounts for a very wide 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. Capabilities of the major ion module of HYDRUS-1D were demonstrated by simulating sodic soil reclamation involving the removal of excessive salts from a soil profile and replacement of exchangeable Na^+ with Ca^{2+} . Capabilities of HP1 were shown by means of example problems involving the leaching of heavy metals subject to

multiple cation exchange reactions and the transport of TNT and its daughter products 2ADNT, 4ADNT, and TAT. This example indicates that ground water may be more vulnerable to leaching of TNT daughter products, notably TAT, than of the parent compound itself and that monitoring for the daughter products may provide an early warning of possible TNT leaching.

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