

Simulating Nonequilibrium Movement of Water, Solutes and Particles Using HYDRUS – A Review of Recent Applications

Jiří ŠIMŮNEK¹, J. MAXIMILIAN KÖHNE², RADKA KODEŠOVÁ³ and MIROSLAV ŠEJNA⁴

¹*Department of Environmental Sciences, University of California, Riverside, USA;*

²*Department of Soil Physics, Helmholtz Centre for Environmental Research, Halle (Saale), Germany;* ³*Department of Soil Science and Geology, Czech University of Life Sciences in Prague, Prague, Czech Republic;* ⁴*PC-Progress, Prague, Czech Republic*

Abstract: Water and contaminants moving through the vadose zone are often subject to a large number of simultaneous physical and chemical nonequilibrium processes. Traditional modeling tools for describing flow and transport in soils either do not consider nonequilibrium processes at all, or consider them only separately. By contrast, a wide range of nonequilibrium flow and transport modeling approaches are currently available in the latest versions of the HYDRUS software packages. The formulations range from classical models simulating uniform flow and transport, to relatively traditional mobile-immobile water physical and two-site chemical nonequilibrium models, to more complex dual-permeability models that consider both physical and chemical nonequilibrium. In this paper we briefly review recent applications of the HYDRUS models that used these nonequilibrium features to simulate nonequilibrium water flow (water storage in immobile domains and/or preferential water flow in structured soils with macropores and other preferential flow pathways), and transport of solutes (pesticides and other organic compounds) and particles (colloids, bacteria and viruses) in the vadose zone.

Keywords: nonequilibrium flow and transport; physical nonequilibrium; chemical nonequilibrium; numerical models; preferential flow; reactive transport; HYDRUS; review of recent applications

It is a pleasure to contribute to the special issue honoring Prof. Kutílek on his 80th birthday. Prof. Kutílek was teaching Hydropedology (a branch of science only recently discovered in US, e.g., LIN *et al.* 2005) at the Czech Technical University in Prague, Czech Republic, when I (the senior author) was a student there in the early 1980's. His entertaining and well-thought out lectures, and especially his earlier books (KUTÍLEK 1978, 1984), attracted me to Soil Physics, to which I later devoted my professional career.

Much has changed since then. Not only our society, but also the tools that we use today to address the

various topics in Soil Physics, including water flow and solute transport, are very different. The knowledge in Soil Physics has vastly increased. There are excellent textbooks available providing an overview of the field to students and professionals alike (e.g., KUTÍLEK & NIELSEN 1994). Moreover, while Prof. Kutílek's lectures and books were primarily devoted to descriptions of various soil physical processes and their governing equations, which were usually solved using relatively complex analytical and semi-analytical models, today, when it is hard to imagine that IBM PC was introduced only about 25 years ago, water flow and solute transport equations are

Supported by the Czech Science Foundation, Projects No. GACR 103/05/2143 and GACR 526/08/0434.

typically solved numerically. Numerical methods dramatically expanded our ability to solve complex mathematical systems involving a large number of simultaneous nonlinear processes that were previously unsolvable. One example is nonequilibrium preferential flow and transport. Computer models based on numerical solutions are now increasingly used for a wide range of applications in the research and management of natural subsurface systems. The wide usage of numerical models was also significantly promoted by their availability in both the public and commercial domains, and by the development of sophisticated graphics-based interfaces that tremendously simplify their use (ŠIMŮNEK 2005).

The HYDRUS software packages (ŠIMŮNEK *et al.* 1998, 2005, 2007, 2008) are among the most widely used models simulating water flow and solute transport in soils. For example, in March of 2007 HYDRUS-1D was downloaded more than 200 times by users from 30 different countries, over one thousand times in 2006, and the HYDRUS web site receives on average some 700 individual visitors each day (ŠIMŮNEK *et al.* 2008). Traditionally, the HYDRUS software, as well as many other models simulating variably saturated water flow and solute transport, either did not consider nonequilibrium flow and transport processes at all or only considered them separately. For example, previous versions of HYDRUS codes considered physical and chemical nonequilibrium separately. Physical nonequilibrium solute transport was accounted for by assuming a two-region, dual-porosity type formulation that partitions the liquid phase into mobile and immobile regions (e.g., VAN GENUCHTEN & WIERENGA 1976). Chemical nonequilibrium solute transport was accounted for by assuming a two-site sorption model, which assumes that sorption sites can be divided into two fractions with sorption to different fractions of sorption sites being either instantaneous or kinetic (e.g., VAN GENUCHTEN & WAGENET 1989).

Over the years, several publicly available numerical codes have been developed that consider a number of options for simulating nonequilibrium water flow and/or solute transport (e.g., PRUESS 1991; JARVIS 1994; VAN DAM *et al.* 1997; KÖHNE *et al.* 2008a, b). Unique to the most recent version of the HYDRUS-1D software package (ŠIMŮNEK *et al.* 2005, 2008) is the wide range of approaches that can be selected for simulating nonequilibrium processes (ŠIMŮNEK & VAN GENUCHTEN 2008).

The models range from classical models simulating uniform flow and transport, to traditional dual-porosity physical and two-site chemical nonequilibrium models, to complex dual-permeability models that consider both physical and chemical nonequilibrium.

While the large number of physical and chemical nonequilibrium approaches available in the latest version of HYDRUS-1D was reviewed previously by ŠIMŮNEK and VAN GENUCHTEN (2008), in this paper we briefly review some recent applications of the HYDRUS models that used these nonequilibrium features to simulate nonequilibrium water flow and solute transport in the vadose zone.

HYDRUS software packages

There are three different versions of the HYDRUS software packages currently in use. HYDRUS-1D (ŠIMŮNEK *et al.* 2005), HYDRUS-2D (ŠIMŮNEK *et al.* 1998), and HYDRUS (2D/3D) (ŠEJNA & ŠIMŮNEK 2007; ŠIMŮNEK *et al.* 2007). While each model considers similar basic processes, their main difference lies in the dimensionality of the problems they can address. While HYDRUS-1D considers one-dimensional problems associated with, for example, soil columns, lysimeters, soil profiles and plots, HYDRUS-2D solves two-dimensional or axisymmetrical three-dimensional problems as encountered on the lab or field scale, and HYDRUS (2D/3D) calculates both two- and three-dimensional problems. HYDRUS (2D/3D) is an upgrade and extension of HYDRUS-2D. In addition to basic water flow and solute transport processes, individual HYDRUS packages can also consider some additional processes. For example, HYDRUS-1D can also consider the transport and production of carbon dioxide (ŠIMŮNEK & SUAREZ 1993) and the transport of major ions and major ion chemistry (ŠIMŮNEK & SUAREZ 1994; GONÇALVES *et al.* 2006), and HYDRUS (2D/3D) can simulate processes in constructed wetlands (LANGERGRABER & ŠIMŮNEK 2005, 2006).

Nonequilibrium flow and transport models

Physical nonequilibrium – mobile-immobile water model

As already discussed, all HYDRUS codes traditionally consider physical and chemical nonequilibrium separately. Physical nonequilibrium solute transport is accounted for by assuming a two-re-

gion, dual-porosity type formulation that partitions the liquid phase (i.e., the total water content θ) into mobile (flowing, inter-aggregate), θ_{mo} , and immobile (stagnant, intra-aggregate), θ_{im} , regions (e.g., VAN GENUCHTEN & WIERENGA 1976):

$$\theta = \theta_{mo} + \theta_{im} \quad (1)$$

While water flow is assumed to be uniform in this model and the immobile water content to be constant with time (i.e., there is no water transfer between two regions), the mobile-immobile water concept, and thus physical nonequilibrium, is applied only to solute transport.

Chemical nonequilibrium – two-site sorption model

Much like the mobile-immobile water concept (MIM), the concept of two-site sorption (TSS) (e.g., VAN GENUCHTEN & WAGENET 1989; model (b) in Figure 1) was already implemented in earlier versions of HYDRUS to permit consideration of nonequilibrium adsorption-desorption reactions. The two-site sorption concept assumes that the sorption sites, s , can be divided into two fractions:

$$s = s^e + s^k \quad (2)$$

Sorption, s^e , on one fraction of the sites (type-1 sites) is assumed to be instantaneous, while sorption, s^k , on the remaining (type-2) sites is assumed to be a first-order rate kinetic process. Parameter f (a fraction of sorption sites at equilibrium with the solution) was used to discriminate between the extent of instantaneous and kinetic sorption.

Additional chemical nonequilibrium models

While the two-site sorption model could always be simplified into a model with only instantaneous ($f = 1$) or kinetic ($f = 0$) sorption (one kinetic site model; model (a) in Figure 1), there was an urgent need for a more complex sorption model for simulating transport of particles in porous media. The more complex, two kinetic sites model (model (c) in Figure 1) was implemented into HYDRUS by SCHIJVEN and ŠIMŮNEK (2002) and ŠIMŮNEK *et al.* (2005). They also reformulated the traditional first-order sorption model

$$\frac{\delta s^k}{\delta t} = \alpha [s^e - s^k] \quad (3)$$

using the concept of attachment/detachment

$$\rho \frac{\delta s^k}{\delta t} = k_a \theta c - k_d \rho s^k \quad (4)$$

In equations (3) and (4), s^e is the sorbed concentration that would be reached at equilibrium with the liquid phase concentration, s^k is the sorbed concentration of the kinetic sorption sites, α is a first-order rate constant describing the kinetics of the sorption process, k_a is the attachment coefficient, k_d is the detachment coefficients, ρ is the bulk density, and c is the liquid phase concentration. ŠIMŮNEK and VAN GENUCHTEN (2008) showed that equations (3) and (4) are mathematically equivalent. However, the attachment/detachment model not only allowed for different attachment and detachment coefficients for the two sorption sites, but also allowed for different interpretation of those sites. That means that different processes could occur at the two sorption sites.

The HYDRUS model that took into account two kinetic sites was first used by SCHIJVEN and ŠIMŮNEK (2002), who simulated the removal of bacteriophages MS2 and PRD1 by dune recharge and removal of MS2 by deep well injection. They argued that the solid phase can be divided into two fractions with different surface properties and various attachment and detachment rate coefficients, reflecting the different surface characteristics of the soil organic carbon and ferric oxyhydroxide.

A different interpretation for the two sorption processes was presented by BRADFORD *et al.* (2002, 2003, 2006a, b). They used the first sorption site to represent the attachment/detachment process and the second sorption site to represent the straining process of colloids. BRADFORD *et al.* (2003, 2006a) used a Langmuir-type blocking (a coefficient ψ that multiplies k_a) for the attachment/detachment sites and depth-dependent blocking for straining sites. Both of these blocking mechanisms render Eq. (4) nonlinear. While BRADFORD *et al.* (2002, 2003) simulated transport of colloidal microspheres in homogeneous soil columns using HYDRUS-1D, BRADFORD *et al.* (2004) used HYDRUS-2D to evaluate the effects of interfacial areas between various heterogeneities on colloid transport. This series of studies ultimately led to the development of a new straining model with a depth dependent blocking function (BRADFORD *et al.* 2006a).

BRADFORD *et al.* (2006b) further used HYDRUS-1D in order to simulate transport and straining of *E. coli* O157:H7 (bacteria significantly larger than colloids) in saturated porous media. For this study, HYDRUS-1D was modified to accommodate a

Physical Equilibrium and Nonequilibrium Models

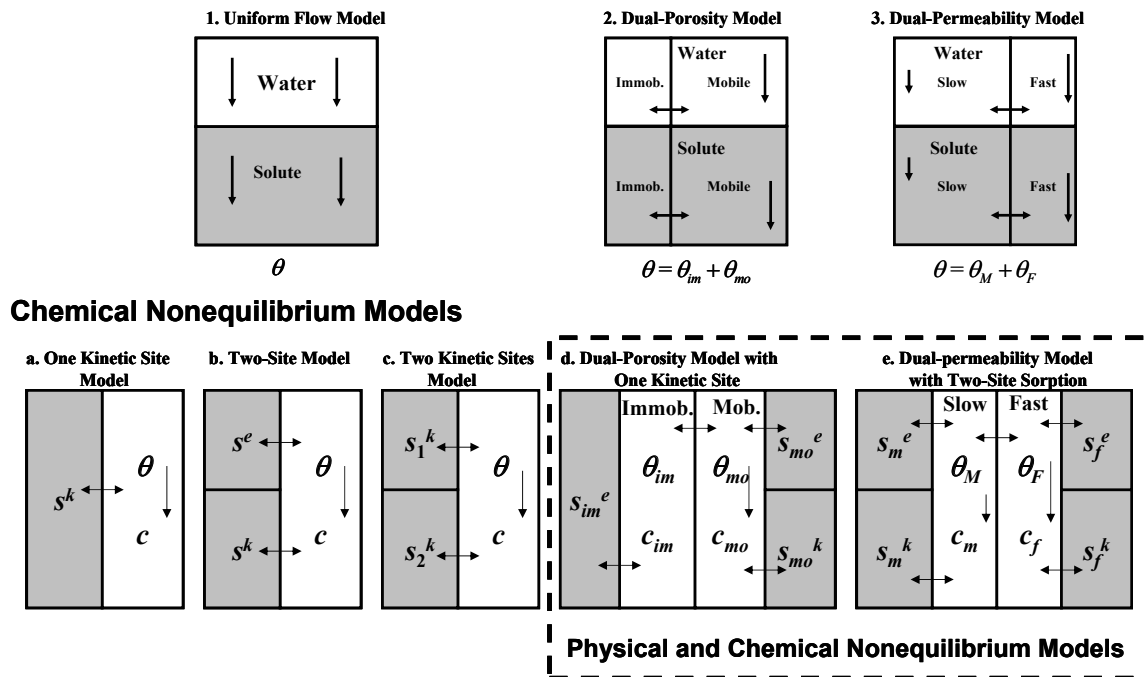


Figure 1. Physical and chemical nonequilibrium models considered by HYDRUS-1D.

newly developed conceptual model that assumed that *E. coli* will aggregate when large numbers of monodispersed *E. coli* are deposited at pore constrictions or straining sites. When the deposited *E. coli* reach a critical concentration at the straining site, the aggregated *E. coli* O157:H7 will be released into the aqueous solution as a result of hydrodynamic shearing forces.

In a series of papers, GARGIULO *et al.* (2007a, b, 2008) used the two kinetic sites model in HYDRUS-1D to simulate the transport and deposition of two bacteria strains (*Deinococcus Radiodurans* and *Rhodococcus rhodochrous*) under both saturated and unsaturated conditions. While the role of bacteria surface hydrophobicity was studied by GARGIULO *et al.* (2008), the role of the matrix grain size and the bacteria surface protein was evaluated by GARGIULO *et al.* (2007b), and the effect of metabolic activity (metabolically active and stationary phase *Deinococcus Radiodurans*) was analyzed by GARGIULO *et al.* (2007a). In all three studies, HYDRUS-1D provided an excellent tool for evaluating various factors involved in the transport and deposition of bacteria in soils.

Additional physical nonequilibrium models

ŠIMŮNEK *et al.* (2003) added two additional options to HYDRUS-1D for simulating nonequi-

librium preferential flow. The simpler model extended the mobile-immobile water concept by assuming that the immobile water content can, like the mobile water content, be transient, and that there can be a water transfer between these two domains (model (2) in Figure 1). They also implemented GERKE and VAN GENUCHTEN's (1993) full dual-permeability model. The dual-permeability model assumes that the porous medium consists of two overlapping pore domains, with water flowing relatively fast in one domain (often called the macropore, fracture, or inter-porosity domain, subscripts *f* and *F*) when close to full saturation, and slow in the other domain (often referred to as the micropore, matrix, or intra-porosity domain, subscript *m* and *M*) (model (3) in Figure 1):

$$\theta = \theta_F + \theta_M = w\theta_f + (1 - w)\theta_m \quad (5)$$

Lower case subscripts in the dual-permeability model refer to the local (pore-region) scale, while upper case subscripts refer to the global (total soil medium) scale. The dual-permeability model was extended further by assuming that the liquid phase of the matrix can be further partitioned into mobile (flowing), $\theta_{mo,m}$, and immobile (stagnant), $\theta_{im,m}$, regions as follows:

$$\theta_m = \theta_{mo,m} + \theta_{im,m} \quad (6)$$

where:

θ_m – volumetric water content of the matrix pore system (POT *et al.* 2005; ŠIMŮNEK & VAN GENUCHTEN 2008).

Examples of applications of dual-porosity models to a range of laboratory and field data involving transient flow and solute transport are provided by ŠIMŮNEK *et al.* (2001), ABBASI *et al.* (2003a, b), CASTIGLIONE *et al.* (2003), KÖHNE *et al.* (2004a, 2006a) and HAWS *et al.* (2005).

ABBASI *et al.* (2003a, b) applied both equilibrium and nonequilibrium (the dual-porosity model) models in HYDRUS-2D to simulate water flow and tracer movement at a sandy loam field plot with furrows (3 m × 3 m) in Phoenix, Arizona, USA. Soil hydraulic and solute transport parameters were optimized by minimizing the objective function defined using water contents, infiltration rates, and solute concentrations. The similarity of the results obtained assuming equilibrium and nonequilibrium flow and transport led to the conclusion that equilibrium transport prevailed at this field site (ABBASI *et al.* 2003a, b).

The MIM approach in HYDRUS-1D was used by KÖHNE *et al.* (2004a) for inverse simulation of pressure heads, water contents, water outflow and Br breakthrough in the effluent of six aggregated soil columns with different initial water contents subject to intermittent irrigations. The physical nonequilibrium was more pronounced for wet and dry soils than for intermediate initial water contents. Inverse identification of the required MIM parameters was fairly successful, except for the saturated water contents in mobile and immobile regions, which were highly correlated (KÖHNE *et al.* 2004a).

Water and solute fluxes from the subsurface drains of two macroporous silty clay loam plots (48.5 m × 60 m) in agricultural fields in West Lafayette, Indiana, were simulated using HYDRUS-2D by HAWS *et al.* (2005). The drainage fluxes (hydrographs) were matched reasonably well by both uniform and dual-porosity (MIM) models. However, a model calibrated on drainage fluxes could not reproduce solute breakthrough. HAWS *et al.* (2005) concluded that a hydrograph fit does not guarantee a proper description of flow patterns at the field scale, and that consideration of solute breakthrough is needed to derive physically meaningful model parameters.

KÖHNE *et al.* (2006a) made similar conclusions based on their field study at the Infeld site in North-West Germany. The observed rapid Br effluent breakthrough at low concentrations could only be simulated using the MIM approach in HYDRUS-2D. Simulation results suggested that over 60% of the surface applied Br was immobilized by transfer into the stagnant soil water region, and that the two-dimensional flow field induced by tile drains enhanced Br dispersion (KÖHNE *et al.* 2006a).

A version of HYDRUS-1D that considers GERKE and VAN GENUCHTEN's (1993) dual-permeability flow and transport model was used in the studies of ŠIMŮNEK *et al.* (2001), ZHANG *et al.* (2004), KÖHNE *et al.* (2004b, 2006b, c), POT *et al.* (2005), DOUSSET *et al.* (2007) and KODEŠOVÁ *et al.* (2006a, b, 2008), among many others.

ZHANG *et al.* (2004) used the dual-permeability model to analyze solute and colloidal tracer tests in laboratory columns that examined the hydraulic properties of a foamed zeolite/iron pellet material that was developed for *in situ* remediation of contaminated groundwater. The colloidal microspheres (1 µm diameter) moved through the columns at a much faster rate than the nonreactive solute tracer tritiated water, reflecting the inter-pellet preferential flow paths in the packed material. Inverse modeling of the microsphere data using a physical nonequilibrium transport model yielded the immobile water content (θ_{im}) equivalent to the intra-pellet porosity (0.40), suggesting that the microspheres were excluded from the small intra-pellet pores and could only move through the large inter-pellet pore spaces. The dual-permeability dual-porosity model also indicated that 6–11% of the total porosity was preferential flow porosity, consistent with the observation of enhanced microsphere transport with respect to tritiated water. Forward modeling with the dual-permeability dual-porosity model suggested that the preferential flow porosity will drastically lower contaminant removal efficiency.

POT *et al.* (2005) used all physical nonequilibrium models from HYDRUS-1D to evaluate laboratory column studies under unsaturated steady-state flow conditions generated using several rainfall intensities. POT *et al.* (2005) needed increasingly complex models to describe tracer displacement column experiments for increasing fluxes. Numerical analyses showed that contrasting physical nonequilibrium transport processes occurred for different fluxes. Multiple (three) porosity domains

(dual-permeability model with immobile zone in the matrix) contributed to flow at the highest rainfall intensities, including preferential flow through macropore pathways. Macropores were not active any longer at the intermediate and lowest velocities, and dual-porosity-type models were able to describe the observed preferential transport well.

KÖHNE *et al.* (2006a) studied the feasibility of the inverse (Levenberg-Marquardt) identification of dual-permeability model parameters from a drainage hydrograph. The dual-permeability model implemented in HYDRUS-1D was used to fit hydraulic and transport parameters, either sequentially or simultaneously, using observed tile-drainage hydrographs and Br concentrations. Only the simultaneous fitting procedure was successful in describing Br breakthrough. From these and lab-scale results, it was inferred that a hydrograph alone is insufficient for the inverse identification of soil hydraulic dual-permeability model parameters (KÖHNE *et al.* 2006a).

KÖHNE *et al.* (2006b) used the dual-permeability model to analyze experiments carried out on a laboratory column (80 cm height, 24 cm diam.) designed for hydraulic tomography that provided outflows separately from the matrix and the central cylindrical preferential flow region, as well as pressure heads and water contents in the preferential flow and matrix regions at various positions. KÖHNE *et al.* (2006b) applied one inverse approach that relied on standard (lumped) observations of infiltration and outflow, while another approach considered separate outflows for the matrix and the PF region. Both inverse approaches provided accurate matches of bulk infiltration and outflow. However, the outflows from either the matrix or the preferential flow region could only be described when the dual-permeability model was fit to region-specific outflow data. KÖHNE *et al.* (2006b) concluded that for natural soils where experimental data do not come in a 'separated form' for fast and slow flow regions, the domain-related hydraulic parameters of the dual-permeability model may be difficult to identify from water flow observations alone.

KODEŠOVÁ *et al.* (2006a) used the single-porosity and dual-permeability models in HYDRUS-1D to simulate variably-saturated water movement in clay soils with and without macropores. Numerical simulations of water flow for several scenarios of probable macropore compositions showed a considerable impact of preferential flow on water infiltration in such soils. Results of numerical

simulations showed that cumulative infiltration into the soil with and without macropores may differ by two or more orders of magnitude. Thus, the appropriate models must be used to describe non-equilibrium flow in such soils.

KODEŠOVÁ *et al.* (2006b) carried out a soil micro-morphological study to demonstrate the impact of soil organisms on soil pore structure. They showed the influence of earthworms, enchytraeids and moles on the pore structure of a Greyic Phaeozem by comparing two soil samples either affected or not affected by these organisms. They also studied macropores created by roots and soil microorganisms in a Haplic Luvisol, and subsequently affected by clay coatings. The dual permeability models implemented in HYDRUS-1D were applied to improve the numerical inversion of the multi-step outflow experiment, and to obtain parameters characterizing multimodal soil hydraulic properties.

Finally, KODEŠOVÁ *et al.* (2008) used micromorphological images for (a) characterization of flow domains in three soil types, (b) selection of a proper model for estimation of multimodal soil hydraulic properties from multi-step outflow experiment and ponding infiltration, and (c) numerical simulation of chlorotoluron transport within the soil profile that was experimentally studied in the field. They showed that chlorotoluron was regularly distributed in the highly connected domain of larger pores of Haplic Luvisol, from which it penetrated into the soil aggregates, i.e., zones of immobile water. The highest mobility of chlorotoluron in Greyic Phaeozem was caused by larger capillary pore pathways and sufficient infiltration fluxes that occasionally filled up these pores. The presence of clay coatings in Greyic Phaeozem that restricted water flow and contaminant transport between the macropore and matrix domains was an additional cause for this preferential transport that produced chlorotoluron penetration into deeper depths. Chlorotoluron was less regularly distributed in Haplic Cambisol. Despite the highest infiltration rate, preferential flow only slightly affected the herbicide transport. Large gravitational pores that may dominate water flow and solute transport under saturated conditions were inactive during the monitored period. As a result of complex interactions between meteorological conditions and the soil pore structure, the single- and dual-porosity models described the herbicide behavior in Haplic Luvisol well, while the dual-

permeability model performed better in simulating the herbicide transport in Greyic Phaeozem and Haplic Cambisol.

Physical and chemical nonequilibrium models

However, many transport situations involve not only physical or chemical nonequilibrium, but both nonequilibrium processes occur simultaneously. One obvious example (e.g., ŠIMŮNEK & VAN GENUCHTEN 2008) occurs during transport through an aggregated laboratory soil column involving steady-state water flow when both a conservative tracer (no sorption) and a reactive solute are used. The collected tracer breakthrough curve may then display a relatively rapid initial breakthrough followed by extensive tailing, which are both features of nonequilibrium transport. Since the tracer is non-reactive, this nonequilibrium must be caused by physical factors. When the reactive solute is also sorbed kinetically to the solid phase (an indication of a chemical nonequilibrium), the use of a model that simultaneously considers both physical and chemical nonequilibrium is required.

HYDRUS offers two options for simulating simultaneous physical and chemical nonequilibrium. The first model, i.e., the dual-porosity model with one kinetic site (model (d) in Figure 1), considers water flow and solute transport in a dual-porosity system, while assuming that sorption in the immobile zone is instantaneous. However, the sorption sites in contact with the mobile zone are now divided into two fractions, subject to either instantaneous or kinetic sorption, similar to the two-site kinetic sorption concept. Since the residence time of solutes in the immobile domain is relatively large, equilibrium likely exists between the solution and the sorption complex here, in which case there is no need to consider kinetic sorption in the immobile domain. On the other hand, the model, assumes the presence of kinetic sorption sites in contact with the mobile zone, since water can move relatively fast in the macropore domain and thus prevent chemical equilibrium (ŠIMŮNEK & VAN GENUCHTEN 2008).

The last nonequilibrium option implemented into HYDRUS-1D combines chemical nonequilibrium with the dual-permeability model (model (e) in Figure 1). This model assumes that equilibrium and kinetic sites exist in both the macropore (fracture) and micropore (matrix) domains. A complete list and more detailed descriptions of

the different models summarized here, including the specific equations used for the water flow and solute transport models, are given in (ŠIMŮNEK & VAN GENUCHTEN 2008).

PANG *et al.* (2008) used the HYDRUS-1D mobile-immobile two-region model with one kinetic site (model (d) in Figure 1) to evaluate the transport of fecal coliforms, *Salmonella* bacteriophage and bromide (Br⁻), in 30 undisturbed lysimeters constructed from undisturbed New Zealand soils. The dual-porosity model considered first-order attachment/detachment and inactivation of the microbes, first-order mass transfer between two regions for Br⁻, and convection and dispersion. Model predictions matched observations reasonably well.

GÄRDENÄS *et al.* (2006) compared four two-dimensional transport models (a uniform flow model, MIM, a dual-porosity model, and a dual-permeability model) in HYDRUS-2D in order to predict preferential water flow and the leaching of the herbicide MCPA in a 50-m long transect through a sloping, heterogeneous, tile-drained field soil in South Sweden. The simulated time covered six weeks following the spray application. Only the dual-permeability and dual-porosity models reproduced the pesticide concentration patterns in drain outflow.

POT *et al.* (2005) used various physical non-equilibrium approaches with kinetic sorption to analyze the impact of different constant rainfall rates on Br⁻, isoproturon and metribuzin leaching in undisturbed soil cores collected from the grassed filter strip. Observations showed a strong impact of rainfall intensity on Br⁻ (see also the text in the previous section) and herbicide leaching. Herbicide transport was affected by kinetic sorption at all flow velocities. Significantly higher estimated values for degradation rate parameters, as compared to batch data, were correlated with the extent of non-equilibrium sorption (POT *et al.* 2005).

Similarly, KÖHNE *et al.* (2006c) applied HYDRUS-1D to simulate the transport of isoproturon, terbuthylazine and Br⁻ observed in an aggregated loamy and a macroporous loamy sand soil column subject to several irrigation-redistribution cycles. The early isoproturon breakthrough in the aggregated loamy soil could be qualitatively predicted when using the dual-permeability model with two-site kinetic sorption. The simulated herbicide breakthrough curves obtained were similar when

either the degradation or sorption rate parameters were optimized. Due to internal parameter correlations and nonuniqueness, inverse model applications could not accurately distinguish between degradation and sorption processes for conditions involving preferential flow.

SUMMARY

In this paper we have summarized a wide range of nonequilibrium water flow and solute transport models that are available in the latest versions of the HYDRUS software packages and reviewed their recent applications. The models range from classical models simulating uniform water flow and solute transport, to traditional mobile-immobile water physical and two-site chemical nonequilibrium models, to more complex dual-permeability models that consider both physical and chemical causes of nonequilibrium.

In general, the most common applications can be divided into two large groups. The first group uses HYDRUS models to simulate transport of colloids, viruses and bacteria, i.e., abiotic and biotic particles in the 0.1 μm to 10 μm size range. These applications usually use the chemical nonequilibrium transport capabilities of the model to simulate processes such as attachment/detachment to the solid phase or air-water interface, or straining. The second group addresses preferential water flow and transport of dissolved chemicals in structured soils with macropores or other preferential flow pathways. For this problem, physical nonequilibrium options are used, sometimes combined with chemical nonequilibrium options, for simulating the transport of pesticides and other organic compounds.

There remains a need for more thorough studies to evaluate how much and what type of information is required to fully parameterize selected nonequilibrium models. Ideally, parameterization would be based on straightforward observations of basic soil structural and physicochemical properties, much in the spirit of Hydropedology, a discipline which lately received renewed attention (LIN *et al.* 2005), and which was always fostered by Prof. Kutílek. Until measurement techniques are fully developed, inverse parameter identification is an indispensable means for the application of complex nonequilibrium models. To facilitate such applications, the objective function for the inverse problem in HYDRUS can be formulated in terms of a large number of variables involving not only

boundary concentration fluxes, but also water and solute distributions within the soil profile and in different phases (ŠIMŮNEK & VAN GENUCHTEN 2008). For these reasons we believe that HYDRUS is a very attractive tool for analyzing both forward and inverse flow and transport problems.

References

- ABBASI F., ŠIMŮNEK J., FEYEN J., VAN GENUCHTEN M.TH., SHOUSE P.J. (2003a): Simultaneous inverse estimation of soil hydraulic and solute transport parameters from transient field experiments: Homogeneous soil. *Transactions of ASAE*, **46**: 1085–1095.
- ABBASI F., JACQUES D., ŠIMŮNEK J., FEYEN, J., VAN GENUCHTEN M.TH. (2003b): Inverse estimation of the soil hydraulic and solute transport parameters from transient field experiments: Heterogeneous soil. *Transactions of ASAE*, **46**: 1097–1111.
- BRADFORD S.A., YATES S.R., BETTEHAR M., ŠIMŮNEK J. (2002): Physical factors affecting the transport and fate of colloids in saturated porous media. *Water Resources Research*, **38**: 1327, doi:10.1029/2002WR001340, 63.1–63.12.
- BRADFORD S.A., ŠIMŮNEK J., BETTEHAR M., VAN GENUCHTEN M.TH., YATES S.R. (2003): Modeling colloid attachment, straining, and exclusion in saturated porous media. *Environmental Science and Technology*, **37**: 2242–2250.
- BRADFORD S.A., BETTEHAR M., ŠIMŮNEK J., VAN GENUCHTEN M.TH. (2004): Straining and attachment of colloids in physically heterogeneous porous media. *Vadose Zone Journal*, **3**: 384–394.
- BRADFORD S.A., ŠIMŮNEK J., BETTAHAR M., VAN GENUCHTEN M.TH., YATES S.R. (2006a): Significance of straining in colloid deposition: evidence and implications. *Water Resources Research*, **42**: W12S15, doi:10.1029/2005WR004791, 16 pp.
- BRADFORD S.A., ŠIMŮNEK J., WALKER S.L. (2006b): Transport and straining of *E. coli* O157:H7 in saturated porous media. *Water Resources Research*, **42**: W12S12, doi:10.1029/2005WR004805, 12 pp.
- CASTIGLIONE P., MOHANTY B.P., SHOUSE P.J., ŠIMŮNEK J., VAN GENUCHTEN M.TH., SANTINI A. (2003): Lateral water diffusion in an artificial macroporous system: Theory and experimental evidence. *Vadose Zone Journal*, **2**: 212–221.
- DOUSSET S., THEVENOT M., POT V., ŠIMŮNEK J., ANDREUX F. (2007): Evaluating equilibrium and non-equilibrium transport of bromide and isoproturon in disturbed and undisturbed soil columns. *Journal of Contaminant Hydrology*, **94**: 261–276.

- GÄRDENÄS A., ŠIMŮNEK J., JARVIS N., VAN GENUCHTEN M.TH. (2006): Two-dimensional modelling of preferential water flow and pesticide transport from a tile-drained field. *Journal of Hydrology*, **329**: 647–660.
- GARGIULO G., BRADFORD S.A., ŠIMŮNEK J., USTOHAL P., VERECKEN H., KLUMPP E. (2007a): Transport and deposition of metabolically active and stationary phase *Deinococcus radiodurans* in unsaturated porous media. *Environmental Science and Technology*, **41**: 1265–1271.
- GARGIULO G., BRADFORD S.A., ŠIMŮNEK J., USTOHAL P., VERECKEN H., KLUMPP E. (2007b): Bacteria transport and deposition under unsaturated conditions: the role of the matrix grain size and the bacteria surface protein. *Journal of Contaminant Hydrology*, **92**: doi:10.1016/j.jconhyd.2007.01.009, 255–273.
- GARGIULO G., BRADFORD S.A., ŠIMŮNEK J., USTOHAL P., VERECKEN H., KLUMPP E. (2008): Bacteria transport and deposition under unsaturated conditions: the role of bacteria surface hydrophobicity. *Vadose Zone Journal*, **7**: 406–419.
- GERKE H.H., VAN GENUCHTEN M.TH. (1993): A dual-porosity model for simulating the preferential movement of water and solutes in structured porous media. *Water Resources Research*, **29**: 305–319.
- GONÇALVES M.C., ŠIMŮNEK J., RAMOS T.B., MARTINS J.C., NEVES M.J., PIRES F.P. (2006): Multicomponent solute transport in soil lysimeters irrigated with waters of different quality. *Water Resources Research*, **42**: W08401, doi:10.1029/2006WR004802, 17 pp.
- HAWS N.W., RAO P.S.C., ŠIMŮNEK J., POYER I.C. (2005): Single-porosity and dual-porosity modeling of water flow and solute transport in subsurface-drained fields using effective field-scale parameters. *Journal of Hydrology*, **313**: 257–273.
- JARVIS N.J. (1994): The MACRO Model (Version 3.1), Technical Description and Sample Simulations. Reports and Dissertations 19, Dept. Soil Sci., Swedish Univ. Agric. Sci., Uppsala.
- KODEŠOVÁ R., KOZÁK J., ŠIMŮNEK J. (2006a): Numerical study of macropore impact on ponded infiltration in clay soils. *Soil and Water Research*, **1**: 16–22.
- KODEŠOVÁ R., KODEŠ V., ŽIGOVÁ A., ŠIMŮNEK J. (2006b): Impact of plant roots and soil organisms on soil micro-morphology and hydraulic properties. *Biologia*, **61** (Suppl. 19): S339–S343.
- KODEŠOVÁ R., KOČÁREK M., KODEŠ V., ŠIMŮNEK J., KOZÁK J. (2008): Impact of soil micromorphological features on water flow and herbicide transport in soils. *Vadose Zone Journal* (Special Issue “Vadose Zone Modeling”), **7**. (in press)
- KÖHNE J.M., KÖHNE S., MOHANTY B.P., ŠIMŮNEK J. (2004a): Inverse mobile-immobile modeling of transport during transient flow: Effect of between-domain transfer and initial water content. *Vadose Zone Journal*, **3**: 1309–1321.
- KÖHNE J.M., MOHANTY B., ŠIMŮNEK J., GERKE H.H. (2004b): Numerical evaluation of a second-order water transfer term for variably saturated dual-permeability models. *Water Resources Research*, **40**: doi:10.1029/2004WR00385.
- KÖHNE S., LENNARTZ B., KÖHNE J.M., ŠIMŮNEK J. (2006a): Bromide transport at a tile-drained field site: experiment, one- and two-dimensional equilibrium and non-equilibrium numerical modeling. *Journal of Hydrology*, **321**: 390–408.
- KÖHNE J.M., MOHANTY B.P., ŠIMŮNEK J. (2006b): Inverse dual-permeability modeling of preferential water flow in a soil column and implications on field-scale solute transport prediction. *Vadose Zone Journal*, **5**: 59–76.
- KÖHNE J.M., KÖHNE S., ŠIMŮNEK J. (2006c): Multi-process herbicide transport in structured soil columns: experiment and model analysis. *Journal of Contaminant Hydrology*, **85**: 1–32.
- KÖHNE J.M., KÖHNE S., ŠIMŮNEK J. (2008a): A review of model applications for structured soils: (a) water flow and tracer transport. *Journal of Contaminant Hydrology*, Special Issue “Flow Domains”. (submitted)
- KÖHNE J.M., KÖHNE S., ŠIMŮNEK J. (2008b): A review of model applications for structured soils: (b) pesticide transport. *Journal of Contaminant Hydrology*, Special Issue “Flow Domains”. (submitted)
- KUTÍLEK M. (1978): *Water Management Soil Science*. SNTL, Praha. (in Czech)
- KUTÍLEK M. (1984): *Moisture of Porous Materials*. SNTL, Praha. (in Czech)
- KUTILEK M., NIELSEN D.R. (1994): *Soil Hydrology*. Catena Verlag, Cremlingen.
- LANGERGRABER G., ŠIMŮNEK J. (2005): Modeling variably-saturated water flow and multi-component reactive transport in constructed wetlands. *Vadose Zone Journal*, **4**: 924–938.
- LANGERGRABER G., ŠIMŮNEK J. (2006): 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.
- LIN H., BOUMA J., WILDING L.P., RICHARDSON J.L., KUTÍLEK M., NIELSEN D.R. (2005): Advances in hydropedology. *Advances in Agronomy*, **85**: 1–97.
- PANG L., MCLEOD M., AISLABIE J., ŠIMŮNEK J., CLOSE M., HECTOR R. (2008): Modeling transport of fecal coliforms and *Salmonella* bacteriophage in ten undisturbed

- New Zealand soils under dairy shed effluent irrigation. *Vadose Zone Journal*, 7: 97–111.
- POT V., ŠIMŮNEK J., BENOIT P., COQUET Y., YRA A., MARTÍNEZ-CORDÓN M.-J. (2005): Impact of rainfall intensity on the transport of two herbicides in undisturbed grassed filter strip soil cores. *Journal of Contaminant Hydrology*, 81: 63–88.
- PRUESS K. (1991): Tough2 – A General-purpose Numerical Simulator for Multiphase Fluid and Heat Flow. Rep. LBL-29400, Lawrence Berkeley Laboratory, Berkeley.
- SCHIJVEN J., ŠIMŮNEK J. (2002): Kinetic modelling of virus transport at field scale. *Journal of Contaminant Hydrology*, 55: 113–135.
- ŠEJNA M., ŠIMŮNEK J. (2007): HYDRUS (2D/3D): Graphical User Interface for the HYDRUS Software Package Simulating Two- and Three-Dimensional Movement of Water, Heat, and Multiple Solutes in Variably-Saturated Media. Published online at www-pc-progress.cz, PC-Progress, Prague.
- ŠIMŮNEK J. (2005): Chapter 78: models of water flow and solute transport in the unsaturated zone. In: ANDERSON M.G., McDONNELL J.J. (eds): *Encyclopedia of Hydrological Sciences*. John Wiley & Sons, Ltd., Chichester, 1171–1180.
- ŠIMŮNEK J., SUAREZ D.L. (1993): Modeling of carbon dioxide transport and production in soil: 1. Model development. *Water Resources Research*, 29: 487–497.
- ŠIMŮNEK J., SUAREZ D.L. (1994): Two-dimensional transport model for variably saturated porous media with major ion chemistry. *Water Resources Research*, 30: 1115–1133.
- ŠIMŮNEK J., VAN GENUCHTEN M.TH. (2008): Modeling nonequilibrium flow and transport with HYDRUS. *Vadose Zone Journal* (Special Issue “Vadose Zone Modeling”), 7. (in press)
- ŠIMŮNEK J., ŠEJNA M., VAN GENUCHTEN M.TH. (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, Colorado.
- ŠIMŮNEK J., WENDROTH O., WYPLER N., VAN GENUCHTEN M.TH. (2001): Nonequilibrium water flow characterized from an upward infiltration experiment. *European Journal of Soil Science*, 52: 13–24.
- ŠIMŮNEK J., JARVIS N.J., VAN GENUCHTEN M.TH., GÄRDENÄS A. (2003): Review and comparison of models for describing non-equilibrium and preferential flow and transport in the vadose zone. *Journal of Hydrology*, 272: 14–35.
- ŠIMŮNEK J., VAN GENUCHTEN M.TH., ŠEJNA M. (2005): The HYDRUS-1D Software Package for Simulating the One-dimensional Movement of Water, Heat, and Multiple Solutes in Variably-saturated Media. Version 3.0. HYDRUS Software Series 1, Department of Environmental Sciences, University of California Riverside, Riverside.
- ŠIMŮNEK J., VAN GENUCHTEN M.TH., ŠEJNA M. (2007): The HYDRUS Software Package for Simulating Two- and Three-Dimensional Movement of Water, Heat, and Multiple Solutes in Variably-Saturated Media. Technical Manual. Version 1.0. PC Progress, Prague.
- ŠIMŮNEK J., VAN GENUCHTEN M.TH., ŠEJNA M. (2008): Development and applications of the HYDRUS and STANMOD software packages, and related codes. *Vadose Zone Journal* (Special Issue “Vadose Zone Modeling”), 7. (in press)
- SUAREZ D.L., ŠIMŮNEK J. (1993): Modeling of carbon dioxide transport and production in soil: 2. Parameter selection, sensitivity analysis and comparison of model predictions to field data. *Water Resources Research*, 29: 499–513.
- VAN DAM J.C., HUYGEN J., WESSELING J.G., FEDDES R.A., KABAT P., VAN VALSUM P.E.V., GROENENDIJK P., VAN DIEPEN C.A. (1997): Theory of SWAP. Version 2.0. Simulation of Water Flow, Solute Transport and Plant Growth in the Soil-Water-Atmosphere-Plant Environment. Technical Document 45, Dept. Water Resources, WAU, Report 71, DLO Winand Staring Centre, Wageningen.
- VAN GENUCHTEN M.TH., WIERENGA P.J. (1976): Mass transfer studies in sorbing porous media, I. Analytical solutions. *Soil Science Society of America Journal*, 40: 473–481.
- VAN GENUCHTEN M.TH., WAGENET R.J. (1989): Two-site/two-region models for pesticide transport and degradation: Theoretical development and analytical solutions. *Soil Science Society of America Journal*, 53: 1303–1310.
- ZHANG P., ŠIMŮNEK J., BOWMAN R.S. (2004): Nonideal transport of solute and colloidal tracers through reactive zeolite/iron pellets. *Water Resources Research*, 40: doi:10.1029/2003WR002445.

Corresponding author:

Prof. JIŘÍ ŠIMŮNEK, University of California, Department of Environmental Sciences, 900 University Avenue, Riverside, CA 92521, USA
tel./fax: +1 951 8277854, e-mail: jiri.simunek@ucr.edu
