

1 **Simulating Nonequilibrium Movement of Water, Solutes and**
2 **Particles Using HYDRUS: A Review of Recent Applications**

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4 **Jiří Šimůnek¹, J. Maximilian Köhne², Radka Kodešová³, Miroslav Šejna⁴**

5 ¹Department of Environmental Sciences, University of California, Riverside, 900 University
6 Avenue, Riverside, CA 92521, USA, jiri.simunek@ucr.edu

7 ²Department of Soil Physics, Helmholtz Centre for Environmental Research, Theodor-Lieser-
8 Straße 4, D-06120 Halle (Saale), Germany

9 ³Department of Soil Science and Geology, Czech University of Life Sciences, Prague,
10 Kamýcká 129, 16521 Prague, Czech Republic

11 ⁴PC-Progress, s.r.o., Anglická 28, 120 00 Prague, Czech Republic

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17 **Abstract**

18 Water and contaminants moving through the vadose zone are often subject to a large number
19 of simultaneous physical and chemical nonequilibrium processes. Traditional modeling tools
20 for describing flow and transport in soils either do not consider nonequilibrium processes at
21 all, or consider them only separately. By contrast, a wide range of nonequilibrium flow and
22 transport modeling approaches are currently available in the latest versions of the HYDRUS
23 software packages. The formulations range from classical models simulating uniform flow
24 and transport, to relatively traditional mobile-immobile water physical and two-site chemical
25 nonequilibrium models, to more complex dual-permeability models that consider both

26 physical and chemical nonequilibrium. In this paper we briefly review recent applications of
27 the HYDRUS models that used these nonequilibrium features to simulate nonequilibrium
28 water flow (water storage in immobile domains and/or preferential water flow in structured
29 soils with macropores and other preferential flow pathways), and transport of solutes
30 (pesticides and other organic compounds) and particles (colloids, bacteria and viruses) in the
31 vadose zone.

32 **Key words:** nonequilibrium flow and transport, physical nonequilibrium, chemical
33 nonequilibrium, numerical models, preferential flow, reactive transport, HYDRUS, review of
34 recent applications

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36 **Introduction**

37 It is a pleasure to contribute to the special issue honoring Prof. Kutílek on his 80th
38 birthday. Prof. Kutílek was teaching Hydropedology (a branch of science only recently
39 discovered in US, e.g., LIN et al. 2005) at the Czech Technical University in Prague, Czech
40 Republic, when I (the senior author) was a student there in the early 1980's. His entertaining
41 and well-thought out lectures, and especially his earlier books (KUTÍLEK 1980, 1982),
42 attracted me to Soil Physics, to which I later devoted my professional career.

43 Much has changed since then. Not only our society, but also the tools that we use
44 today to address the various topics in Soil Physics, including water flow and solute transport,
45 are very different. The knowledge in Soil Physics has vastly increased. There are excellent
46 textbooks available providing an overview of the field to students and professionals alike
47 (e.g., KUTÍLEK & NIELSEN 1994). Moreover, while Prof. Kutílek's lectures and books were
48 primarily devoted to descriptions of various soil physical processes and their governing
49 equations, which were usually solved using relatively complex analytical and semi-analytical
50 models, today, when it is hard to imagine that IBM PC was introduced only about 25 years

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

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

75 Over the years, several publicly available numerical codes have been developed that

76 consider a number of options for simulating nonequilibrium water flow and/or solute transport
77 (e.g., PRUESS 1991; JARVIS 1994; VAN DAM *et al.* 1997; KÖHNE *et al.* 2008ab). Unique to the
78 most recent version of the HYDRUS-1D software package (ŠIMŮNEK *et al.* 2005, 2008) is the
79 wide range of approaches that can be selected for simulating nonequilibrium processes
80 (ŠIMŮNEK & VAN GENUCHTEN 2008). The models range from classical models simulating
81 uniform flow and transport, to traditional dual-porosity physical and two-site chemical
82 nonequilibrium models, to complex dual-permeability models that consider both physical and
83 chemical nonequilibrium.

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

89

90

HYDRUS Software Packages

91 There are three different versions of the HYDRUS software packages currently in use.
92 HYDRUS-1D (ŠIMŮNEK *et al.* 2005), HYDRUS-2D (ŠIMŮNEK *et al.* 1998), and HYDRUS
93 (2D/3D) (ŠIMŮNEK *et al.* 2006; ŠEJNA & ŠIMŮNEK 2007). While each model considers similar
94 basic processes, their main difference lies in the dimensionality of the problems they can
95 address. While HYDRUS-1D considers one-dimensional problems associated with, for
96 example, soil columns, lysimeters, soil profiles and plots, HYDRUS-2D solves two-
97 dimensional or axisymmetrical three-dimensional problems as encountered on the lab or field
98 scale, and HYDRUS (2D/3D) calculates both two- and three-dimensional problems.
99 HYDRUS (2D/3D) is an upgrade and extension of HYDRUS-2D. In addition to basic water
100 flow and solute transport processes, individual HYDRUS packages can also consider some

101 additional processes. For example, HYDRUS-1D can also consider the transport and
102 production of carbon dioxide (ŠIMŮNEK & SUAREZ 1993) and the transport of major ions and
103 major ion chemistry (ŠIMŮNEK & SUAREZ 1994; GONÇALVES *et al.* 2007), and HYDRUS
104 (2D/3D) can simulate processes in constructed wetlands (LANGERGRABER & ŠIMŮNEK 2005,
105 2006).

106

107 **Nonequilibrium Flow and Transport Models**

108 **Physical Nonequilibrium – Mobile-Immobile Water Model**

109 As already discussed, all HYDRUS codes traditionally consider physical and chemical
110 nonequilibrium separately. Physical nonequilibrium solute transport is accounted for by
111 assuming a two-region, dual-porosity type formulation that partitions the liquid phase (i.e., the
112 total water content θ) into mobile (flowing, inter-aggregate), θ_{mo} , and immobile (stagnant,
113 intra-aggregate), θ_{im} , regions (e.g., VAN GENUCHTEN & WIERENGA 1976):

$$114 \quad \theta = \theta_{mo} + \theta_{im} \quad (1)$$

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

118

119 **Chemical Nonequilibrium – Two-Site Sorption Model**

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

$$125 \quad s = s^e + s^k \quad (2)$$

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

130

131 **Additional Chemical Nonequilibrium Models**

132 While the two-site sorption model could always be simplified into a model with only
133 instantaneous ($f=1$) or kinetic ($f=0$) sorption (one kinetic site model; model (a) in Figure 1),
134 there was an urgent need for a more complex sorption model for simulating transport of
135 particles in porous media. The more complex, two kinetic sites model (model (c) in Figure 1)
136 was implemented into HYDRUS by SCHIJVEN and ŠIMŮNEK (2002) and ŠIMŮNEK *et al.*
137 (2005). They also reformulated the traditional first-order sorption model

$$138 \quad \frac{\partial s^k}{\partial t} = \alpha [s_e^k - s^k] \quad (3)$$

139 using the concept of attachment/detachment

$$140 \quad \rho \frac{\partial s^k}{\partial t} = k_a \theta c - k_d \rho s^k \quad (4)$$

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

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

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

167 BRADFORD *et al.* (2006b) further used HYDRUS-1D in order to simulate transport and
168 straining of *E. coli* O157:H7 (bacteria significantly larger than colloids) in saturated porous
169 media. For this study, HYDRUS-1D was modified to accommodate a newly developed
170 conceptual model that assumed that *E. coli* will aggregate when large numbers of
171 monodispersed *E. coli* are deposited at pore constrictions or straining sites. When the
172 deposited *E. coli* reach a critical concentration at the straining site, the aggregated *E. coli*
173 O157:H7 will be released into the aqueous solution as a result of hydrodynamic shearing
174 forces.

175 In a series of papers, GARGIULO *et al.* (2007ab, 2008) used the two kinetic sites model
176 in HYDRUS-1D to simulate the transport and deposition of two bacteria strains (*Deinococcus*
177 *Radiodurans* and *Rhodococcus rhodochrous*) under both saturated and unsaturated conditions.
178 While the role of bacteria surface hydrophobicity was studied by GARGIULO *et al.* (2008), the
179 role of the matrix grain size and the bacteria surface protein was evaluated by GARGIULO *et al.*
180 (2007b), and the effect of metabolic activity (metabolically active and stationary phase
181 *Deinococcus Radiodurans*) was analyzed by GARGIULO *et al.* (2007a). In all three studies,
182 HYDRUS-1D provided an excellent tool for evaluating various factors involved in the
183 transport and deposition of bacteria in soils.

184

185 **Additional Physical Nonequilibrium Models**

186 ŠIMŮNEK *et al.* (2003) added two additional options to HYDRUS-1D for simulating
187 nonequilibrium preferential flow. The simpler model extended the mobile-immobile water
188 concept by assuming that the immobile water content can, like the mobile water content, be
189 transient, and that there can be a water transfer between these two domains (model (2) in
190 Figure 1). They also implemented GERKE and VAN GENUCHTEN's (1993) full dual-
191 permeability model. The dual-permeability model assumes that the porous medium consists of
192 two overlapping pore domains, with water flowing relatively fast in one domain (often called
193 the macropore, fracture, or inter-porosity domain, subscripts f and F) when close to full
194 saturation, and slow in the other domain (often referred to as the micropore, matrix, or intra-
195 porosity domain, subscript m and M) (model (3) in Figure 1):

$$196 \quad \theta = \theta_f + \theta_M = w\theta_f + (1-w)\theta_m \quad (5)$$

197 Lower case subscripts in the dual-permeability model refer to the local (pore-region) scale,
198 while upper case subscripts refer to the global (total soil medium) scale. The dual-
199 permeability model was extended further by assuming that the liquid phase of the matrix can

200 be further partitioned into mobile (flowing), $\theta_{mo,m}$, and immobile (stagnant), $\theta_{im,m}$, regions as
201 follows:

$$202 \quad \theta_m = \theta_{mo,m} + \theta_{im,m} \quad (6)$$

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

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

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

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

223 Water and solute fluxes from the subsurface drains of two macroporous silty clay loam
224 plots (48.5 m × 60 m) in agricultural fields in West Lafayette, Indiana, were simulated using

225 HYDRUS-2D by HAWS *et al.* (2005). The drainage fluxes (hydrographs) were matched
226 reasonably well by both uniform and dual-porosity (MIM) models. However, a model
227 calibrated on drainage fluxes could not reproduce solute breakthrough. HAWS *et al.* (2005)
228 concluded that a hydrograph fit does not guarantee a proper description of flow patterns at the
229 field scale, and that consideration of solute breakthrough is needed to derive physically
230 meaningful model parameters.

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

237 A version of HYDRUS-1D that considers GERKE and VAN GENUCHTEN's (1993) dual-
238 permeability flow and transport model was used in the studies of ŠIMŮNEK *et al.* (2001), ZHANG
239 *et al.* (2004), KÖHNE *et al.* (2004b, 2006bc), and POT *et al.* (2005), KODEŠOVÁ *et al.* (2006ab,
240 2008), among many others.

241 ZHANG *et al.* (2004) used the dual-permeability model to analyze solute and colloidal
242 tracer tests in laboratory columns that examined the hydraulic properties of a foamed
243 zeolite/iron pellet material that was developed for *in situ* remediation of contaminated
244 groundwater. The colloidal microspheres (1 μm diameter) moved through the columns at a
245 much faster rate than the nonreactive solute tracer tritiated water, reflecting the inter-pellet
246 preferential flow paths in the packed material. Inverse modeling of the microsphere data using
247 a physical nonequilibrium transport model yielded the immobile water content (θ_m)
248 equivalent to the intra-pellet porosity (0.40), suggesting that the microspheres were excluded
249 from the small intra-pellet pores and could only move through the large inter-pellet pore

250 spaces. The dual-permeability dual-porosity model also indicated that 6 - 11% of the total
251 porosity was preferential flow porosity, consistent with the observation of enhanced
252 microsphere transport with respect to tritiated water. Forward modeling with the dual-
253 permeability dual-porosity model suggested that the preferential flow porosity will drastically
254 lower contaminant removal efficiency.

255 POT *et al.* (2005) used all physical nonequilibrium models from HYDRUS-1D to
256 evaluate laboratory column studies under unsaturated steady-state flow conditions generated
257 using several rainfall intensities. POT *et al.* (2005) needed increasingly complex models to
258 describe tracer displacement column experiments for increasing fluxes. Numerical analyses
259 showed that contrasting physical nonequilibrium transport processes occurred for different
260 fluxes. Multiple (three) porosity domains (dual-permeability model with immobile zone in the
261 matrix) contributed to flow at the highest rainfall intensities, including preferential flow
262 through macropore pathways. Macropores were not active any longer at the intermediate and
263 lowest velocities, and dual-porosity-type models were able to describe the observed
264 preferential transport well.

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

273 KÖHNE *et al.* (2006b) used the dual-permeability model to analyze experiments carried
274 out on a laboratory column (80 cm height, 24 cm diam.) designed for hydraulic tomography

275 that provided outflows separately from the matrix and the central cylindrical preferential flow
276 region, as well as pressure heads and water contents in the preferential flow and matrix
277 regions at various positions. KÖHNE *et al.* (2006b) applied one inverse approach that relied on
278 standard (lumped) observations of infiltration and outflow, while another approach considered
279 separate outflows for the matrix and the PF region. Both inverse approaches provided
280 accurate matches of bulk infiltration and outflow. However, the outflows from either the
281 matrix or the preferential flow region could only be described when the dual-permeability
282 model was fit to region-specific outflow data. KÖHNE *et al.* (2006b) concluded that for natural
283 soils where experimental data do not come in a ‘separated form’ for fast and slow flow
284 regions, the domain-related hydraulic parameters of the dual-permeability model may be
285 difficult to identify from water flow observations alone.

286 KODEŠOVÁ *et al.* (2006a) used the single-porosity and dual-permeability models in
287 HYDRUS-1D to simulate variably-saturated water movement in clay soils with and without
288 macropores. Numerical simulations of water flow for several scenarios of probable macropore
289 compositions showed a considerable impact of preferential flow on water infiltration in such
290 soils. Results of numerical simulations showed that cumulative infiltration into the soil with
291 and without macropores may differ by two or more orders of magnitude. Thus, the
292 appropriate models must be used to describe non-equilibrium flow in such soils.

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

300 parameters characterizing multimodal soil hydraulic properties.

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

320

321 **Physical and Chemical Nonequilibrium Models**

322 However, many transport situations involve not only physical or chemical
323 nonequilibrium, but both nonequilibrium processes occur simultaneously. One obvious
324 example (e.g., ŠIMŮNEK & VAN GENUCHTEN 2008) occurs during transport through an

325 aggregated laboratory soil column involving steady-state water flow when both a conservative
326 tracer (no sorption) and a reactive solute are used. The collected tracer breakthrough curve
327 may then display a relatively rapid initial breakthrough followed by extensive tailing, which
328 are both features of nonequilibrium transport. Since the tracer is non-reactive, this
329 nonequilibrium must be caused by physical factors. When the reactive solute is also sorbed
330 kinetically to the solid phase (an indication of a chemical nonequilibrium), the use of a model
331 that simultaneously considers both physical and chemical nonequilibrium is required.

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

344 The last nonequilibrium option implemented into HYDRUS-1D combines chemical
345 nonequilibrium with the dual-permeability model (model (e) in Figure 1). This model assumes
346 that equilibrium and kinetic sites exist in both the macropore (fracture) and micropore
347 (matrix) domains. A complete list and more detailed descriptions of the different models
348 summarized here, including the specific equations used for the water flow and solute transport
349 models, are given in (ŠIMŮNEK & VAN GENUCHTEN 2008).

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

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

362 POT *et al.* (2006) used various physical nonequilibrium approaches with kinetic
363 sorption to analyze the impact of different constant rainfall rates on Br⁻, isoproturon and
364 metribuzin leaching in undisturbed soil cores collected from the grassed filter strip.
365 Observations showed a strong impact of rainfall intensity on Br⁻ (see also the text in the
366 previous section) and herbicide leaching. Herbicide transport was affected by kinetic sorption
367 at all flow velocities. Significantly higher estimated values for degradation rate parameters, as
368 compared to batch data, were correlated with the extent of non-equilibrium sorption (POT *et*
369 *al.*, 2005).

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

375 breakthrough curves obtained were similar when either the degradation or sorption rate
376 parameters were optimized. Due to internal parameter correlations and nonuniqueness,
377 inverse model applications could not accurately distinguish between degradation and sorption
378 processes for conditions involving preferential flow.

379

380 **Summary**

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

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

396 There remains a need for more thorough studies to evaluate how much and what type
397 of information is required to fully parameterize selected nonequilibrium models. Ideally,
398 parameterization would be based on straightforward observations of basic soil structural and
399 physicochemical properties, much in the spirit of Hydropedology, a discipline which lately

400 received renewed attention (LIN *et al.* 2005), and which was always fostered by Prof. Kutílek.
401 Until measurement techniques are fully developed, inverse parameter identification is an
402 indispensable means for the application of complex nonequilibrium models. To facilitate such
403 applications, the objective function for the inverse problem in HYDRUS can be formulated in
404 terms of a large number of variables involving not only boundary concentration fluxes, but
405 also water and solute distributions within the soil profile and in different phases (ŠIMŮNEK &
406 VAN GENUCHTEN 2008). For these reasons we believe that HYDRUS is a very attractive tool
407 for analyzing both forward and inverse flow and transport problems.

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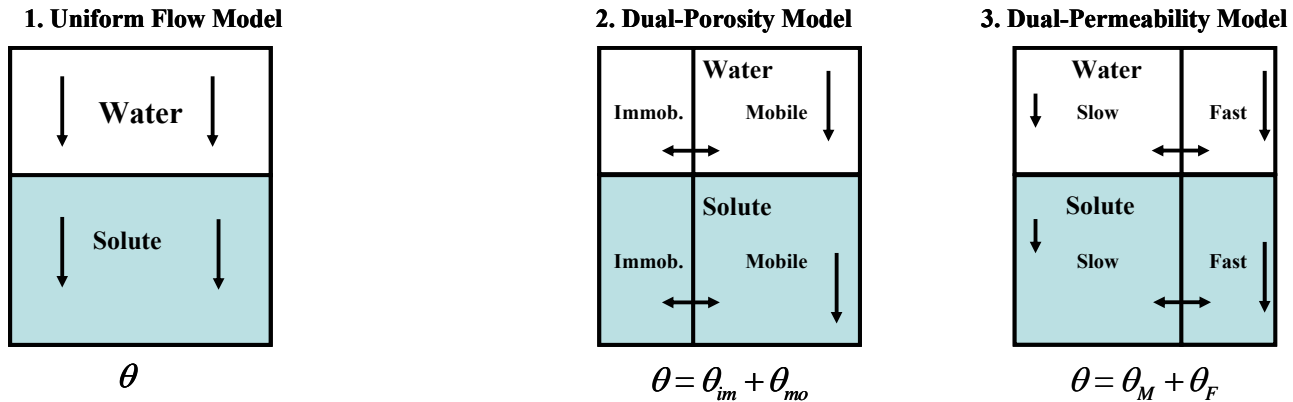
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Physical Equilibrium and Nonequilibrium Models



Chemical Nonequilibrium Models

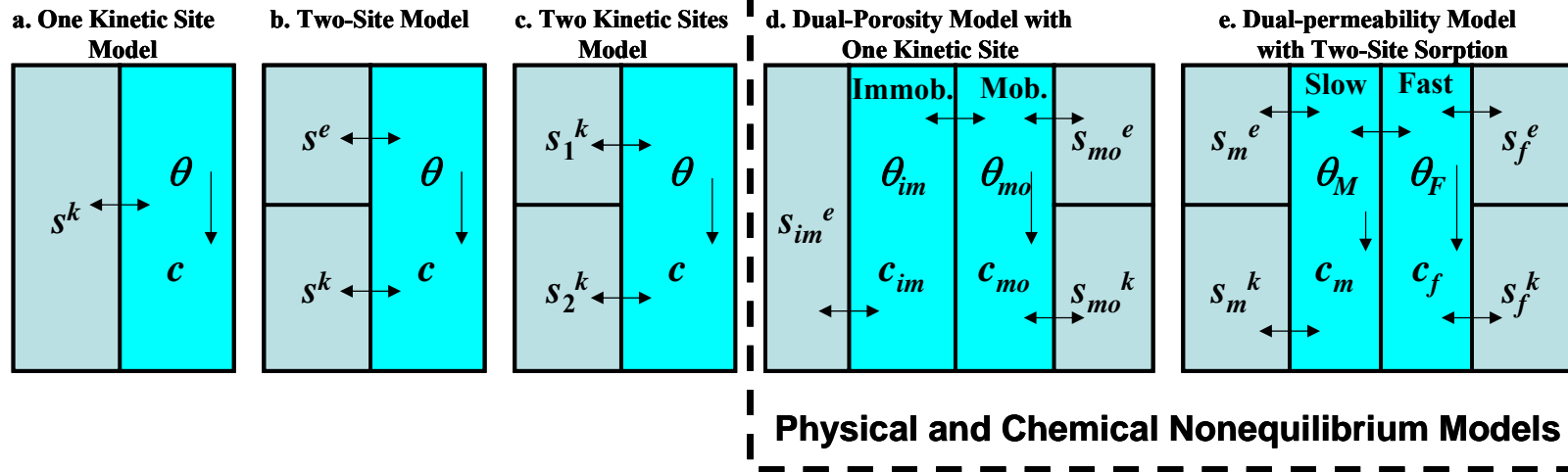


Figure 1. Physical and chemical nonequilibrium models considered by HYDRUS-1D.