

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

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16  
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

35

## 36 **Introduction**

37 It is a pleasure to contribute to the special issue honoring Prof. Kutílek on his 80<sup>th</sup>  
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.

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### **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  $\theta$ ) into mobile (flowing, inter-aggregate),  $\theta_{mo}$ , and immobile (stagnant,  
113 intra-aggregate),  $\theta_{im}$ , 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  $\alpha$  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,  $\rho$  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  $\psi$   
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  $\theta_m$  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  $\mu\text{m}$  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 ( $\theta_m$ )  
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<sup>-</sup>, 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<sup>-</sup> (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<sup>-</sup> 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  $\mu\text{m}$  to 10  $\mu\text{m}$  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.

408

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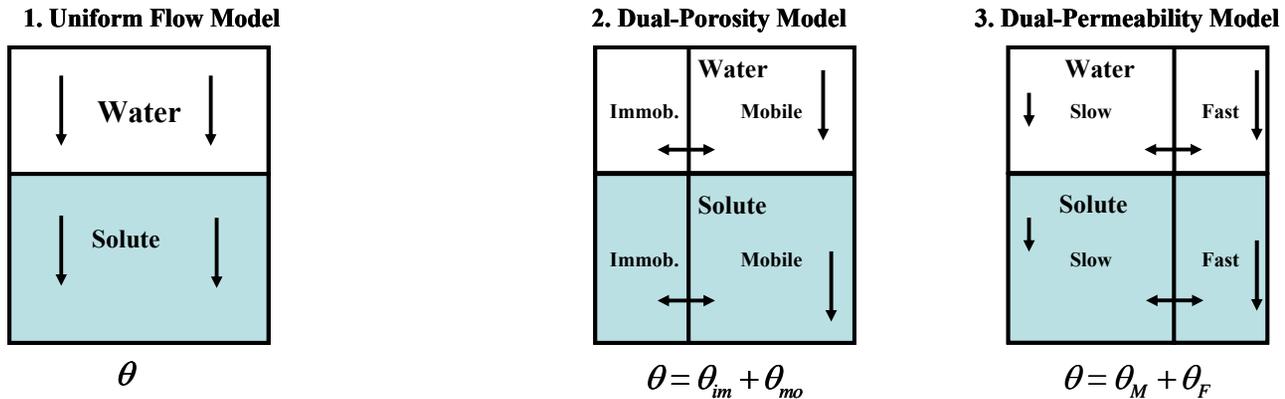
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# Physical Equilibrium and Nonequilibrium Models



# Chemical Nonequilibrium Models

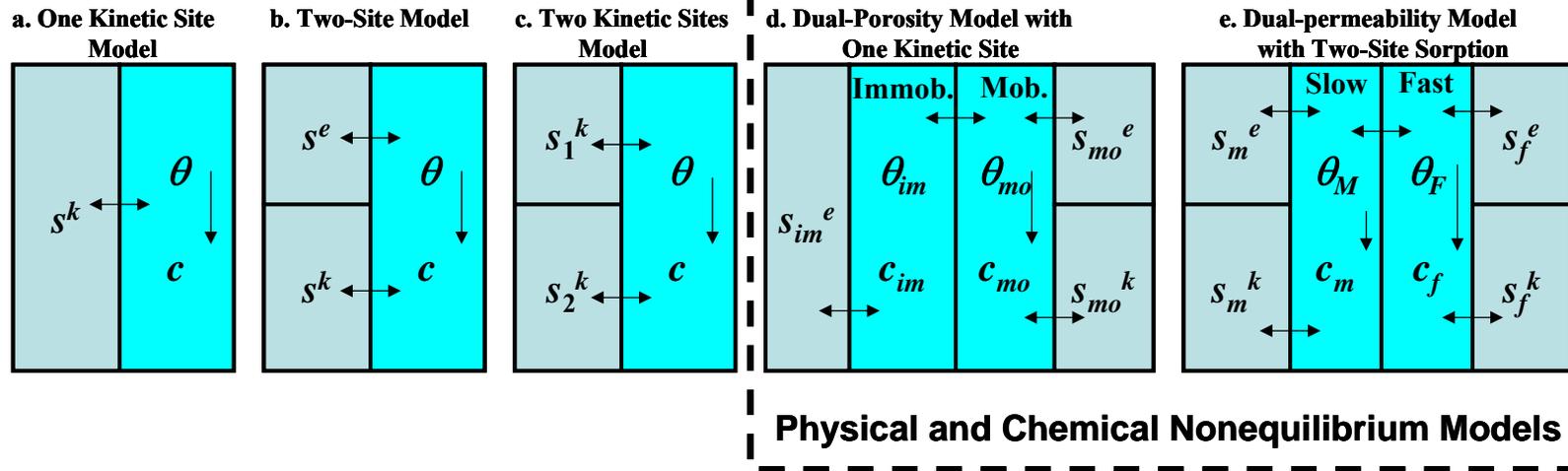


Figure 1. Physical and chemical nonequilibrium models considered by HYDRUS-1D.