

UC Riverside

UC Riverside Previously Published Works

Title

Assessing the Potential Exposure of Groundwater to Pesticides: A Model Comparison

Permalink

<https://escholarship.org/uc/item/6ht5r7k8>

Journal

Vadose Zone Journal, 16(11)

ISSN

1539-1663

Authors

Diamantopoulos, Efstathios
Šimůnek, Jiří
Oberdörster, Christoph
[et al.](#)

Publication Date

2017-11-01

DOI

10.2136/vzj2017.04.0070

Peer reviewed

Original Research

Assessing the Potential Exposure of Groundwater to Pesticides: A Model Comparison

Efstathios Diamantopoulos,* Jiří Šimůnek, Christoph Oberdörster, Klaus Hammel, Bernhard Jene, Tom Schröder, and Thomas Harter

Core Ideas

- Numerical models were compared for transport of four pesticides in nine pedoclimatic scenarios.
- Conceptual uncertainty in soil physical representation of pesticide transport was assessed.
- HYDRUS (2D/3D) can be used as an alternative model for pesticide assessment studies.

E. Diamantopoulos, Institute of Geoecology, Soil Science and Soil Physics Division, Technische Univ. Braunschweig, 38106 Braunschweig, Germany; E. Diamantopoulos and T. Harter, Dep. of Land, Air, and Water Resources, Univ. of California, Davis, CA 95616; J. Šimůnek, Dep. of Environmental Sciences, Univ. of California, Riverside, CA 92521; C. Oberdörster and K. Hammel, Bayer AG, Germany; B. Jene and T. Schröder, BASF SE, 67117 Limburgerhof, Germany. *Corresponding author (ediamant@ucdavis.edu).

Received 5 Apr. 2017.
Accepted 18 Aug. 2017.

Citation: Diamantopoulos, E., J. Šimůnek, C. Oberdörster, K. Hammel, B. Jene, T. Schröder, and T. Harter. 2017. Assessing the potential exposure of groundwater to pesticides: A model comparison. *Vadose Zone J.* 16(11). doi:10.2136/vzj2017.04.0070

Vol. 16, Iss. 11, 2017
© Soil Science Society of America
5585 Guilford Rd., Madison, WI 53711 USA.
All rights reserved.

Many pesticide-leaching studies rely on the use of numerical models that account for various physicochemical and biological processes at a range of temporal and spatial scales. In leaching assessments for the registration of pesticides in the European Union and the United States, one-dimensional models are used that describe the vertical transport of soil water and pesticides to groundwater. One-dimensional models are most representative for spray and broadcast applications of pesticides, but they may not be adequate for spatially nonuniform applications such as microdrip irrigation. We tested whether an advanced numerical model capable of one-, two-, and three-dimensional flow and pesticide transport simulation [HYDRUS (2D/3D)] provides results consistent with one-dimensional numerical models commonly used for pesticide registration (PEARL, PELMO). Model comparison was used to assess conceptual uncertainty in soil physical representation of pesticide transport among numerical models across a range of applications. Simulations of soil water flow and pesticide and heat transport were conducted for four different hypothetical pesticides and nine European regulatory standard pedoclimatic scenarios (FOCUS). The results show that the predicted annual amount of pesticide mass leached below the depth of 1 m, for all substances, locations, and simulation years, was on the same order of magnitude among the three models. Additionally, the simulated 80th percentile of annual pesticide concentrations at the 1-m depth was not statistically different among models. HYDRUS (2D/3D) can, therefore, be used as an alternative model for pesticide assessment studies and provides a conceptual framework consistent with PEARL and PELMO but capable of two- and three-dimensional applications as well.

Abbreviations: ET, evapotranspiration; PEC, predicted environmental concentration; PM, percolated mass; PW, percolated water.

Pesticides are biocidal chemical substances on which modern agriculture depends for good production results. The fate of pesticides in the unsaturated zone depends on a variety of different physical, chemical, and biological processes in the soil, as well as on the pedoclimatic boundary conditions and the application conditions, such as application type, application timing, and application rate. To avoid unacceptable levels of pesticides in groundwater, a thorough exposure assessment using numerical pesticide leaching models is required in most countries before registration is granted.

In the European Union, an assessment of potential leaching of pesticides and their metabolites to groundwater has been mandatory for the last two decades. For reasons of harmonization, FOCUS (FORum for the Co-ordination of pesticide fate models and their Use) was established in 1993 to facilitate the calculation of predicted environmental concentrations (PEC) of pesticides and other plant protection products. Within this framework, environmental fate models are used in a regulatory context to describe the fate and behavior of pesticides and their metabolites in the vadose zone. Furthermore, FOCUS defined nine realistic worst case scenarios representing conditions in the European Union that are considered vulnerable to leaching. These scenarios include various locations across

Europe and their specific agricultural and pedoclimatic conditions (FOCUS, 2000).

Within the framework of FOCUS (2000), which was amended by FOCUS (2014), four standard models for leaching assessment are available, namely PEARL (Tiktak et al., 2000), PELMO (Klein, 1995), PRZM (Carsel et al., 1998), and MACRO (Jarvis et al., 1991; Larsbo et al., 2005). The PEARL model simulates water flow and heat transport by using the Soil–Water–Atmosphere–Plant (SWAP) model (van Dam et al., 1997). In SWAP, water flow is described by the Richards equation (Richards, 1931), which is numerically solved using an implicit finite difference scheme. For solute transport, PEARL uses the convection–dispersion equation. PELMO and PRZM use the tipping bucket approach (Carsel et al., 1984) to simulate water flow across discrete soil layers and the convection–dispersion equation to simulate solute transport. Both models have been used in various studies on pesticide leaching (Ferrari et al., 2005; Estes et al., 2016; among others). PRZM was later extended to PRZM-3, which includes a module (VADOFT) that also solves the Richards equation for water flow (Carsel et al., 2003). However, this version is not used in a regulatory context. Lastly, MACRO uses the Richards equation to describe water flow in the soil matrix and a kinetic wave equation to describe water flow in the macropore domain (Alaoui et al., 2003). In addition, it uses the convection–dispersion equation for solute transport. Significant differences in numerical models can be found not only in the treatment of flow and transport processes but also in the conceptualization of the driving boundary conditions (root and plant growth, root–water–solute interaction, soil–air interface conditions, soil–groundwater interface conditions).

All models mentioned above are one-dimensional, which limits the consideration of water flow and solute (pesticide) and heat transport to the vertical (z) dimension. This approach is typically representative of spray and broadcast applications of pesticides across large areas on a leveled soil surface. However, some types of agricultural applications, such as drip irrigation (Elmaloglou et al., 2010), furrow irrigation (Deb et al., 2016), seed treatments (Hoesel et al., 2017), or crops grown on ridges, may require a multidimensional description of flow and transport processes near the land surface because water flow is not exclusively vertical or a pesticide application is not uniform across the soil surface. The application of one-dimensional models in such situations may result in inaccurate, overly simplistic predictions of pesticide exposure (Köhne et al., 2006).

HYDRUS (2D/3D) (Šimůnek et al., 2012, 2016) is a general software package for simulating water, heat, and solute movement in one-, two- and three-dimensional variably saturated porous media. It numerically solves the Richards equation for saturated–unsaturated water flow and the convection–dispersion equation for heat and solute transport. The main advantage of HYDRUS is that it can handle multidimensional flow regions delineated by irregular

boundaries. Flow and transport can occur in the vertical plane, the horizontal plane, in a three-dimensional region exhibiting radial symmetry about the vertical axis, or in a fully three-dimensional domain. HYDRUS has been used and tested in various studies concerning water flow and pesticide transport (e.g., Boivin et al., 2006; Abdel-Nasser et al., 2011; Köhne et al., 2009a, 2009b; Šimůnek et al., 2016).

Simulating the application of pesticides to agricultural lands is a complex exercise involving multiple physical, chemical, and biological processes occurring simultaneously. Given the diversity of processes, of their drivers, and of numerical modeling approaches available to represent these, model comparison is a standard simulation code verification method, including cases where numerical models solve some of the same governing equations (Vereecken et al., 2016). Model comparison is also useful for the identification of differing representations in boundary conditions, processes, or process interactions that may cause different model predictions; for studying the range of pesticide leaching predictions to a given forcing; and for studying how model predictions deviate under different forcings. Code verification via model comparison is used to show that different model approaches give the same or similar results, particularly when solving problems that cannot be simulated with analytical methods (Vereecken et al., 2016). From a management perspective, model intercomparison allows new modeling concepts to be evaluated for their predictive capabilities and for expanding their use into more advanced management simulations (Vanderborght et al., 2005; Vanderborght and Vereecken, 2007). Verifying HYDRUS against the standard EU screening models in pesticide leaching studies under conditions given by the FOCUS framework would establish a path toward using HYDRUS to assess pesticide fate and transport for two- and three-dimensional pesticide fate and leaching problems, which the standard EU screening models cannot do.

In this study, we tested the hypotheses that (i) HYDRUS predictions for water flow and pesticide transport are in agreement with the two standard EU regulatory models using the same forcing and matrix flow for water and solute transport as HYDRUS and (ii) differences in code implementation between those models may result in systematic deviation from established results. Specifically, we compared HYDRUS against PEARL and PELMO models to assess pesticide leaching to groundwater under the nine FOCUS standard scenarios (FOCUS, 2000). PEARL is based on the same equations as HYDRUS, while PELMO is an example of a different conceptual approach allowed within FOCUS using a simpler, field capacity approach to describing water dynamics. Differences between PEARL and PELMO provide a range of outcomes permitted under the regulatory permitting approach against which differences in HYDRUS simulations can be quantified. Here we first present the underlying mathematical equations, which are numerically solved in both HYDRUS and PEARL. We then parameterize HYDRUS (2D/3D) based on the nine FOCUS

one-dimensional scenarios. The results from the three environmental models are compared with respect to both water flow and pesticide transport in an agricultural (a single crop) scenario.

Materials and Methods

Numerical Modeling

Here, we focus on the one-dimensional forms of the governing equations. See Šimůnek et al. (2012) for the full three-dimensional forms of the governing equations implemented in HYDRUS (2D/3D). The mathematical equations for PELMO are not presented here; see Klein (1995).

One-dimensional water flow in variably saturated porous media is described in both the HYDRUS and PEARL models using the Richards equation:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[K(b) \left(\frac{\partial b}{\partial z} + 1 \right) \right] - S \quad [1]$$

where θ [$L^3 L^{-3}$] is the volumetric water content, t [T] is time, z [L] is the vertical spatial coordinate, positive upward, b [L] is the pressure head, $K(b)$ [$L T^{-1}$] is the unsaturated hydraulic conductivity function, and S [$L^3 L^{-3} T^{-1}$] is a sink term representing root water uptake.

HYDRUS and PEARL implement the Mualem–van Genuchten model (van Genuchten, 1980) to describe soil hydraulic properties. The soil water retention curve and the unsaturated hydraulic conductivity function are defined by

$$\theta(b) = \begin{cases} \theta_r + (\theta_s - \theta_r) \left(1 + |\alpha b|^n \right)^{-m} & b < 0 \\ \theta_s & b \geq 0 \end{cases} \quad [2]$$

$$S_e = \frac{\theta(b) - \theta_r}{\theta_s - \theta_r} \quad [3]$$

$$K(S_e) = K_s S_e^l \left[1 - \left(1 - S_e^{1/m} \right)^m \right]^2 \quad [4]$$

where θ_s and θ_r [$L^3 L^{-3}$] are the saturated and residual water contents, respectively, α [L^{-1}], n (dimensionless), m (dimensionless), and l (dimensionless) are shape parameters, $m = 1 - 1/n$, $n > 1$, and S_e (dimensionless) is the effective saturation.

In HYDRUS, heat transport is described using a convection–diffusion type equation. If we neglect the effect of vapor diffusion and reduce the problem to one-dimensional vertical transport, it is of the form

$$\frac{\partial C_p(\theta)T}{\partial t} = \frac{\partial}{\partial z} \left[\lambda(\theta) \frac{\partial T}{\partial z} \right] - C_w \frac{\partial q T}{\partial x} - C_w S T \quad [5]$$

where T is temperature [K], $C_p(\theta)$ and C_w are the volumetric heat capacities [$M L^{-1} T^{-2} K^{-1}$] of the porous medium (as a function of the water content θ) and the liquid (water) phase, respectively, q is the volumetric water flux density [$L T^{-1}$], S is the sink term defined in Eq. [1], and $\lambda(\theta)$ is the coefficient of the apparent thermal conductivity of the soil [$M L T^{-3} K^{-1}$]. In contrast, PEARL accounts for only thermal diffusion through the soil profile. In PEARL, the convective heat transport represented by the second term and the third term on the right side of Eq. [5] are omitted. Both $C_p(\theta)$ and $\lambda(\theta)$ functions are required for the numerical solution of Eq. [5]. There are differences between HYDRUS and PEARL in the parametrization of the $C_p(\theta)$ and $\lambda(\theta)$ functions. In HYDRUS, $C_p(\theta)$ is approximated by

$$C_p(\theta) \approx (1.92\theta_n + 2.51\theta_o + 4.18\theta)10^6 \left(J m^{-3} C^{-1} \right) \quad [6]$$

where θ_n and θ_o [$L^3 L^{-3}$] refer to volumetric fractions of the solid phase and organic matter, respectively.

Moreover, $\lambda(\theta)$ is defined as

$$\lambda(\theta) = \lambda_0(\theta) + \beta_c C_w |q| \quad [7]$$

where $\lambda_0(\theta)$ is the thermal conductivity of the porous medium for $q = 0$, and β_c is the thermal dispersivity [L]. In HYDRUS, $\lambda_0(\theta)$ can be described by the models of Chung and Horton (1987) or Campbell (1985). Chung and Horton (1987) represent thermal conductivity as a function of the water content only. Campbell (1985) also accounts for soil composition (percentages of solid, quartz, clay, and other minerals).

PEARL assumes that $C_p(\theta)$ is given by

$$C_p(\theta) = \theta_{\text{sand}} C_{\text{sand}} + \theta_{\text{clay}} C_{\text{clay}} + \theta_o C_o + \theta C_w + \varepsilon C_{\text{air}} \quad [8]$$

where θ_{sand} , θ_{clay} , θ_o , and ε [$L^3 L^{-3}$] are the volumetric fractions of sand, clay, organic matter, and air, and C_{sand} , C_{clay} , C_o , and C_{air} are volumetric heat capacities of the individual components. PEARL computes $\lambda(\theta)$ using the method of Ashby et al. (1996), which accounts for both soil composition and soil geometry (particle shapes).

The transformation of a parent (p) pesticide to its metabolite (d) product, as well as sorption of both species on the soil matrix and degradation in the liquid (w), solid (so), and gas (g) phases, and the one-dimensional transport of the parent pesticide and metabolite products is described in both HYDRUS and PEARL as

$$\begin{aligned} \frac{\partial \theta c_p}{\partial t} + \frac{\partial \rho S_p^{so}}{\partial t} + \frac{\partial a_v g_p}{\partial t} = \\ - \frac{\partial q c_p}{\partial z} + \frac{\partial}{\partial z} \left(\theta D_p^w \frac{\partial c_p}{\partial z} \right) + \frac{\partial}{\partial z} \left(a_v D_p^g \frac{\partial g_p}{\partial z} \right) \\ - \left(\mu_p^w + \mu_p^{so} \right) \theta c_p - \left(\mu_p^{so} + \mu_p^{so} \right) \rho S_p^{so} - \left(\mu_p^g + \mu_p^g \right) a_v g_p \end{aligned} \quad [9]$$

$$\begin{aligned} \frac{\partial \theta c_d}{\partial t} + \frac{\partial \rho S_d^{so}}{\partial t} + \frac{\partial a_v g_d}{\partial t} = \\ - \frac{\partial q c_d}{\partial z} + \frac{\partial}{\partial z} \left(\theta D_d^w \frac{\partial c_d}{\partial z} \right) + \frac{\partial}{\partial z} \left(a_v D_d^g \frac{\partial g_d}{\partial z} \right) - \mu_d^w \theta c_d \\ - \mu_d^{so} \rho S_d^{so} - \mu_d^g a_v g_d + \mu_p^w \theta c_p + \mu_p^{so} \rho S_p^{so} + \mu_p^g a_v g_p \end{aligned} \quad [10]$$

where c , s^{so} , and g are the pesticide concentrations in the liquid [M L⁻³], solid [M M⁻¹], and air phases [M L⁻³], respectively; ρ is the soil bulk density [M L⁻³]; a_v is the air content [L³ L⁻³]; μ^w , μ^{so} , and μ^g are the first-order rate coefficients describing degradation of both species in the liquid, solid, and air phases [T⁻¹], respectively; μ_p^w , μ_p^{so} , and μ_p^g are similar first-order rate coefficients describing the transformation of the parent pesticide to its metabolite [T⁻¹], respectively; D^w refers to the dispersion coefficient [L² T⁻¹] for the liquid phase and D^g to the diffusion coefficient for the air phase [L² T⁻¹].

In HYDRUS, the concentrations in the air phase g and the liquid phase c are related by the linear expression

$$g = k_g c \quad [11]$$

with

$$k_g = \frac{1}{K_H R T_A} \quad [12]$$

where K_H is the Henry's Law constant [M T² M⁻¹ L⁻²], R is the universal gas constant [M L² T⁻² K⁻¹ M⁻¹], and T_A is the absolute temperature [K]. PEARL relates both air and liquid concentrations by assuming an equivalent expression (Tiktak et al., 2000).

For both models, D^w is given by

$$\theta D^w = D_L |q| + \theta D_{\text{pure}}^w \tau_w \quad [13]$$

where D_L is the longitudinal dispersivity [L], D_{pure}^w is the molecular diffusion coefficient in free water [L² T⁻¹], and τ_w is the tortuosity factor in the liquid phase (dimensionless), described in both models by the Millington and Quirk (1961) model.

Similarly,

$$D^g = D_{\text{pure}}^g \tau_g \quad [14]$$

where D_{pure}^g is the molecular diffusion coefficient of the pesticide in the gas phase [L² T⁻¹] and τ_g is the tortuosity factor in the gas phase (dimensionless) (Millington and Quirk, 1961).

Solute sorption on the soil matrix can be described in both models by the Freundlich adsorption equation:

$$S^{so} = K_f c_o \left(\frac{c}{c_o} \right)^{n_f} \quad [15]$$

where K_f [L³ M⁻¹], c_o is a reference concentration (usually 1 mg L⁻¹), and n_f (dimensionless) are empirical coefficients. The value of K_f may strongly depend on various soil properties such as the organic matter content, which can be considered as the main sorbent, and is often approximated by

$$K_f = m_{\text{om}} K_{f,\text{om}} \quad [16]$$

where m_{om} [M M⁻¹] is the organic matter mass content in the soil and $K_{f,\text{om}}$ is the coefficient of equilibrium sorption on organic matter [L³ M⁻¹].

Both HYDRUS and PEARL assume that all transformation and degradation parameters (μ_p^w , μ_p^{so} , μ_p^g and μ^w , μ^{so} , μ^g , respectively), as appear in Eq. [9] and [10], are temperature and water content dependent. The temperature dependence is given by

$$a^T = \alpha_R^T \left[\frac{E_a (T_A - T_R^A)}{R T_A T_R^A} \right] = \alpha_R^T \frac{-E_a}{R} \left(\frac{1}{T^A} - \frac{1}{T_R^A} \right) \quad [17]$$

where α_R^T and a^T are parameter values at a reference absolute temperature T_R^A and absolute temperature T^A , respectively; E_a [M L² T⁻² M⁻¹] is the activation energy of each chemical reaction or process being modeled. Unlike HYDRUS, PEARL assumes that when $T < 0$, $a^T = 0$.

The water content dependence of the transformation and degradation parameters is given by the modified equation of Walker (1974):

$$a^\theta = \alpha_R^\theta \min \left[1, \left(\frac{\theta}{\theta_R^*} \right)^B \right] \quad [18]$$

where α_R^θ and a^θ are parameter values at the reference water content θ_R^* and at the water content θ , respectively, and B is a shape parameter. The value of θ_R^* is calculated for the reference pressure head h_R using Eq. [2].

Boundary Conditions and Parameterization of the Models for the FOCUS Scenarios

Nine standard FOCUS scenarios are described in the main FOCUS groundwater report (FOCUS, 2000). They include nine locations that represent realistic worst cases for pesticide leaching in major agricultural regions and span the range of temperatures and precipitation rates occurring in the European Union's agricultural regions. The nine locations are given in Table 1. The simulation period is 26 yr. The first 6 yr are considered as a warm-up period to create realistic initial water contents, temperatures, and pesticide concentrations. Evaluation of the predicted concentrations is performed for the last 20 yr.

The parameterization of the PEARL and PELMO models is described in the FOCUS groundwater report (FOCUS [2000,

Table 1. Scenarios according to FOCUS (2000), soil classification according to USDA, organic C in the topsoil, and the type of lower boundary conditions used in PEARL and HYDRUS at each location.

Scenario	Irrigation	Organic C (20 cm)	Texture (USDA)	Type of lower boundary condition	
				PEARL	HYDRUS
		%			
Châteaudun	✓	1.4	silty clay loam	free drainage	free drainage
Hamburg	–	1.5	sandy loam	flux	deep drainage
Jokioinen	–	4.1	loamy sand	flux	deep drainage
Kremsmünster	–	2.1	loam/silt loam	flux	deep drainage
Okehampton	–	2.2	loam	free drainage	free drainage
Piacenza	–	1.0	loam	time-dependent groundwater position	time-variable pressure head
Porto	✓	3.8	loam	flux	deep drainage
Sevilla	✓	0.9	silt loam	time-dependent groundwater position	time-variable pressure head
Thiva	✓	0.8	loam	free drainage	free drainage

Appendices C and E] and in FOCUS [2014] for the new scenarios of Porto and Piacenza).

HYDRUS Parameterization and Boundary Conditions Relative to PEARL

Using HYDRUS (2D/3D), we assumed a two-dimensional domain with a width of 1 cm (to obtain an approximate one-dimensional domain as used by the other models) and a depth of 450 cm (except for Sevilla, where a 600-cm domain was used). The discretization of the triangular finite element grid in the z direction was equal to 1 cm, except for the top 1 cm, which was divided into four triangular elements, each with 0.5-cm vertical thickness. This resulted in a total number of 904 nodes (except for the Sevilla profile, which had 1204 nodes). The soil properties in the horizontal direction were assumed to be homogeneous to mimic a one-dimensional domain. The parameter values required to describe the soil hydraulic properties (Eq. [2–4]) of all soil layers in each scenario are given in FOCUS (2000). An atmospheric boundary condition was used at the top of the simulation profile: daily precipitation (and irrigation, if relevant, Table 1), potential evaporation (E_p) of water at the soil surface, and potential transpiration (T_p) of water through the plant roots are specified by the user. PEARL splits potential evapotranspiration (ET_p) into E_p and T_p , based on each crop's leaf area index and the soil cover fraction. Daily values of both E_p and T_p were obtained from PEARL. Different bottom boundary conditions for water flow were used in different scenarios.

Table 1 shows the types of bottom boundary conditions for each location used in PEARL and the corresponding lower boundary conditions used in HYDRUS. Free drainage and flux boundary conditions in the case of PEARL are the same as free drainage and deep drainage boundary conditions, respectively, in HYDRUS. In PEARL, the time-dependent groundwater position boundary condition is a special case of a Dirichlet-type boundary condition that accounts for varying, user-specified depth to the water

table. The pressure head at the water table is equal to zero, and the simulation domain is divided into an unsaturated and a saturated domain (Kroes et al., 2008). This type of boundary condition was simulated in HYDRUS using a time-dependent pressure head boundary condition. A no-flow boundary condition was used on the left and right sides of the domain. The initial condition was set to a hydrostatic distribution of pressure head at all locations (FOCUS, 2000).

For the simulation of root water uptake, PEARL calculates a potential water uptake distribution in the root zone, the integral of which is equal to T_p . In the FOCUS scenarios, it is assumed that potential root water uptake is constant throughout the entire root zone, which is defined as the domain between the soil surface and the maximum rooting depth. Due to plant development, the maximum rooting depth is a function of time. The same root water uptake scheme was used in HYDRUS. In both PEARL and HYDRUS, actual root water uptake is derived from potential root water uptake using the model of Feddes et al. (1978). This model reduces the potential root water uptake if the pressure heads in the root zone are outside of an optimum range. It requires five parameters that are only crop specific. The model of Feddes et al. (1978) is also implemented in HYDRUS, and the PEARL parameters defined for a FOCUS crop were directly used in HYDRUS. For all nine scenarios, we considered a potato (*Solanum tuberosum* L.) crop as described in FOCUS (2000).

Heat flow was simulated by assuming a Dirichlet boundary condition at the soil surface. Daily values of temperature at the soil surface were extracted from the PEARL input files and applied in HYDRUS as time-variable temperatures at the soil surface. The lower boundary condition was set equal to a third-type (Cauchy type) boundary condition, which reduces to a second type (Neumann type) when water flow is directed out of the domain. The required thermal conductivities for each soil layer

were obtained from the HYDRUS database according to Chung and Horton (1987). Finally, we assumed that the soil at $t = 0$ is in thermal equilibrium.

For each of the nine scenarios simulated with HYDRUS, the fate of four dummy pesticides in the vadose zone was investigated. The physicochemical properties of these pesticides are described in the FOCUS groundwater report (FOCUS, 2000) as (Table 2):

- A: a medium-persistent, low-sorbing compound that is nonvolatile.
- B: a low-persistent compound that is somewhat volatile.
- C: a low-persistent compound with medium adsorption having a persistent and mobile transformation product (metabolite), denoted as Met-C.
- D: a low-persistent compound that is somewhat volatile, similar to Substance B but with a somewhat stronger adsorption.

For the numerical solution of Eq. [9] and [10], the upper boundary condition was chosen to be a third-type condition accounting for gas diffusion. At the bottom of the soil profile, a zero concentration gradient boundary condition was selected. The soil profile was assumed to be solute-free at time zero. Table 2 shows the sorption and degradation properties for the four hypothetical substances that are the main drivers for leaching (Eq. [9–10]). The Freundlich factor K_f in Eq. [15] was calculated for each substance from Eq. [16], and the Freundlich exponent n was set to 0.9. The degradation coefficients in water, solid, and air phases, μ^w , μ^{so} , and μ^g in Eq. [9–10], were taken equal to $\ln(2)/DT_{50}$, where DT_{50} is the degradation half-life in soil under reference conditions (20°C, the water content at a reference pressure head h_R). To calculate the decay constant for every soil layer, the reference coefficients were multiplied by a depth-specific factor as defined in the FOCUS scenarios (FOCUS, 2000). For the transformation coefficients of Substance C (μ_p^w , μ_p^{so} , and μ_p^g coefficients in Eq. [9–10]), it was assumed that the molar transformation fraction to the metabolite was equal to 1 in all three models. This resulted in a mass

conversion factor of 0.75 due to the differences in the molar mass of 200 g mol⁻¹ for the parent and 150 g mol⁻¹ for the metabolite according to FOCUS (2000).

The vertical longitudinal dispersivity was set equal to 5 cm for all soil layers as defined in the FOCUS scenarios (Eq. [11]). For all substances, we set the value of the molecular diffusion coefficient in free water equal to 0.43 cm² d⁻¹ (Eq. [11]). The molecular diffusion coefficient in soil air was set equal to 0 for Substances A, C, and Met-C since they are not volatile. For Substances B and D, it was set equal to 4300 cm² d⁻¹. For the two slightly volatile substances (B and D), the equilibrium distribution constant between liquid and gaseous phases (dimensionless) was calculated from the substance solubility in water, the substance molecular weight, and its partial vapor pressure. HYDRUS requires the thickness of the stagnant boundary layer at the soil surface through which volatile substances diffuse into the atmosphere, d [L]. This was set to 0.5 cm (Jury et al., [1983]). The activation energy for the temperature dependence (Eq. [17]) of the degradation and transformation coefficients was set equal to 65,400 J mol⁻¹ according to the European Food Safety Authority (2008). For the water content dependence, it was assumed that $B = 0.7$ and $h_R = -100$ cm (Eq. [18]), which corresponds to the water content at field capacity in accordance with FOCUS (2000).

Twenty-six-year simulations were conducted for all nine locations. In terms of water dynamics, the three models were compared in terms of (i) the mean annual actual evapotranspiration (ET_{act}), which is equal to the mean annual actual evaporation of water at the soil surface (E_{act}) and the mean annual actual transpiration (T_{act}) from the plant roots and (ii) the mean annual volume of water percolated below the 1-m depth (PW). For pesticide transport, the annual solute mass percolating below 1 m (PM) was compared. Results are presented only for the following three locations: Kremsmünster, Châteaudun, and Piacenza. These locations use different types of boundary conditions at the lower end of the simulation domain (Table 1). Finally, we present the 80th percentile (PE_w) of the annual volume of water percolated below the 1-m depth and the 80th percentile of the annual flux-averaged pesticide concentrations for the four dummy pesticides at 1 m (PEC_{gw}) for all locations and all three models. We focus mainly on differences between PEARL and HYDRUS (2D/3D) and do not discuss in detail the results of PELMO. More information about the discrepancies between PEARL and PELMO can be found in FOCUS (2000) and FOCUS (2014).

Table 2. Sorption and degradation properties of the four hypothetical substances.

Substance	Main chemical properties			
	K_{om}^\dagger	DT_{50}^\ddagger	Vapor pressure	Solubility
	L kg ⁻¹	d	mPa	mg L ⁻¹
A	60	60	10 ⁻⁷	90
B	10	20	0.1	90
C	100	20	10 ⁻⁷	50
C metabolite	30	100	10 ⁻⁷	90
D	60	20	0.1	90

[†] Freundlich partition coefficient for equilibrium sorption, normalized to organic matter; $K_{om} = K_{oc}/1.724$.

[‡] Degradation half-life in soil under reference conditions (20°C, pF2/water content at field capacity).

Results and Discussion

For the Kremsmünster scenario, annual ET_{act} varies from <400 to about 700 mm (Fig. 1a). HYDRUS ET_{act} values follow the same temporal patterns obtained with PEARL and PELMO but are about 10 to 50 mm higher than the other two models except in 2 yr with exceptionally low ET_{act} . Differences in ET_{act} between

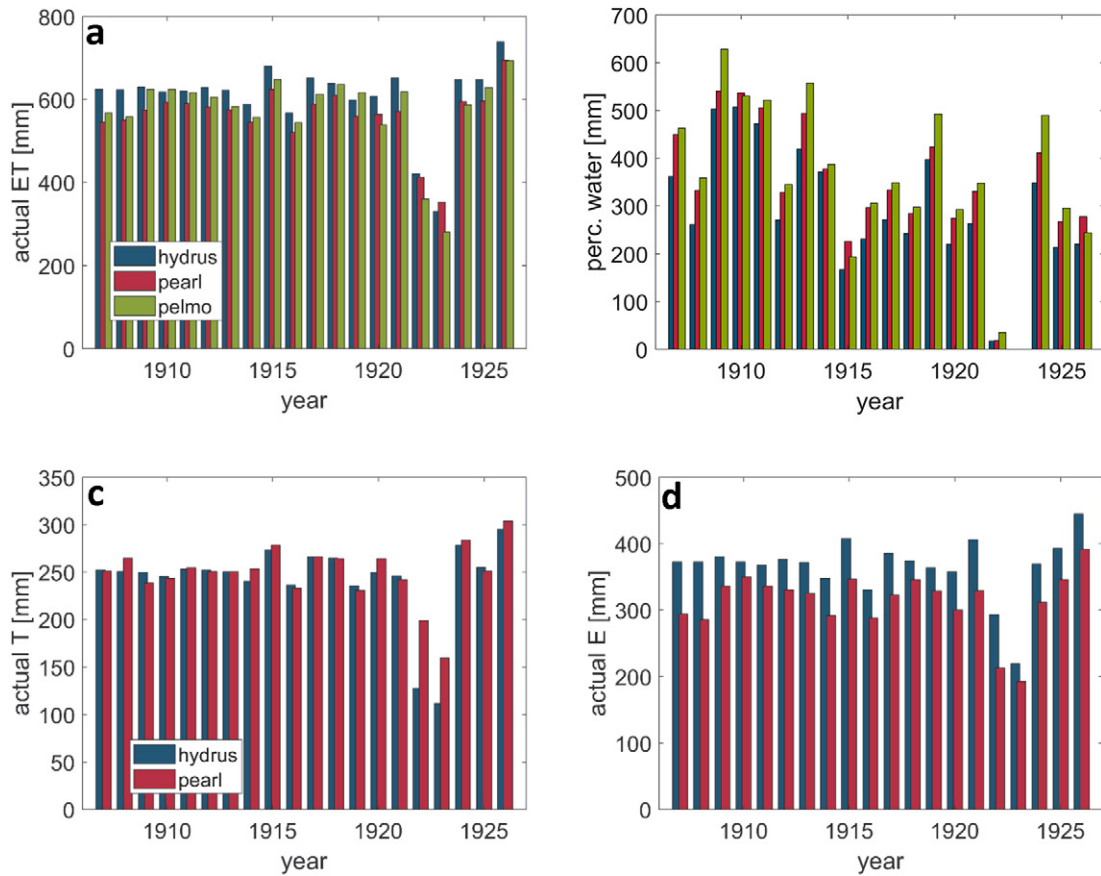


Fig. 1. (a) Annual actual evapotranspiration ET_{act} and (b) annual volumes of water (PW) percolated below the 1-m depth as predicted by the three numerical models (for the Kremsmünster scenario), and (c) annual actual transpiration T_{act} and (d) annual actual evaporation E_{act} as predicted by HYDRUS and PEARL.

PELMO and PEARL are of similar magnitude but more randomly distributed. The resulting PW at 1-m depth, in most years, varies between about 200 and >500 mm, with 2 yr showing nearly negligible PW. Given that precipitation input is identical between the models, the higher ET_{act} in HYDRUS causes a lower PW relative to PEARL (Fig. 1b).

These differences result from different handling of actual soil evaporation between models. Breaking down ET into its two components, actual plant transpiration T_{act} is typically about 250 mm and varies from 100 to 300 mm. Differences between HYDRUS and PEARL are small, <20 mm, except in the low ET years 1922 and 1923, when T_{act} was much lower for HYDRUS than for PEARL (Fig. 1c). In contrast, HYDRUS calculated much higher E_{act} than PEARL, except in the low ET year 1923 (Fig. 1d). HYDRUS applies a Neumann boundary condition at the soil surface when the pressure head is greater than a critical minimum surface pressure head h_{crit} (-10^6 cm in this study). In this case, the actual evaporation flux at the soil surface is equal to potential evaporation. When the soil at the surface becomes drier than h_{crit} , the boundary condition switches from a flux boundary to a Dirichlet boundary condition with $h_{z=0} = h_{crit}$. SWAP, the water transport module in PEARL, sets actual soil evaporation

to potential soil evaporation in wet soils exactly as in HYDRUS. But under dry soil conditions, SWAP limits the evaporation flux to the maximum evaporation rate that the soil can sustain, using the Darcy–Buckingham law at the soil surface. This is achieved by calculating the pressure head gradient between the uppermost node and the atmosphere. However, in SWAP, a further reduction of actual evaporation is introduced by using the approach of Boesten and Stroosnijder (1986), which uses an empirical parameter β ($cm^{1/2}$). This model limits actual evaporation based on the assumption of a specified relationship between cumulative potential and actual evaporation (FOCUS, 2014). This explains the systematically lower soil evaporation values of PEARL compared with HYDRUS and consequently higher percolation, PW, values.

Pesticide mass transport to below the 1-m depth is much more dynamic than the variability in water percolation would suggest. For most substances, the annual mass flux commonly varies by a factor of two to more than an order of magnitude between years (Fig. 2). Between substances, mass flux to below 1 m varies by nearly two orders of magnitude in any given year. Although the PW values calculated by HYDRUS were slightly lower than those of PEARL, the calculated PM values for all substances were consistently 10 to 50% higher with HYDRUS than with PEARL.

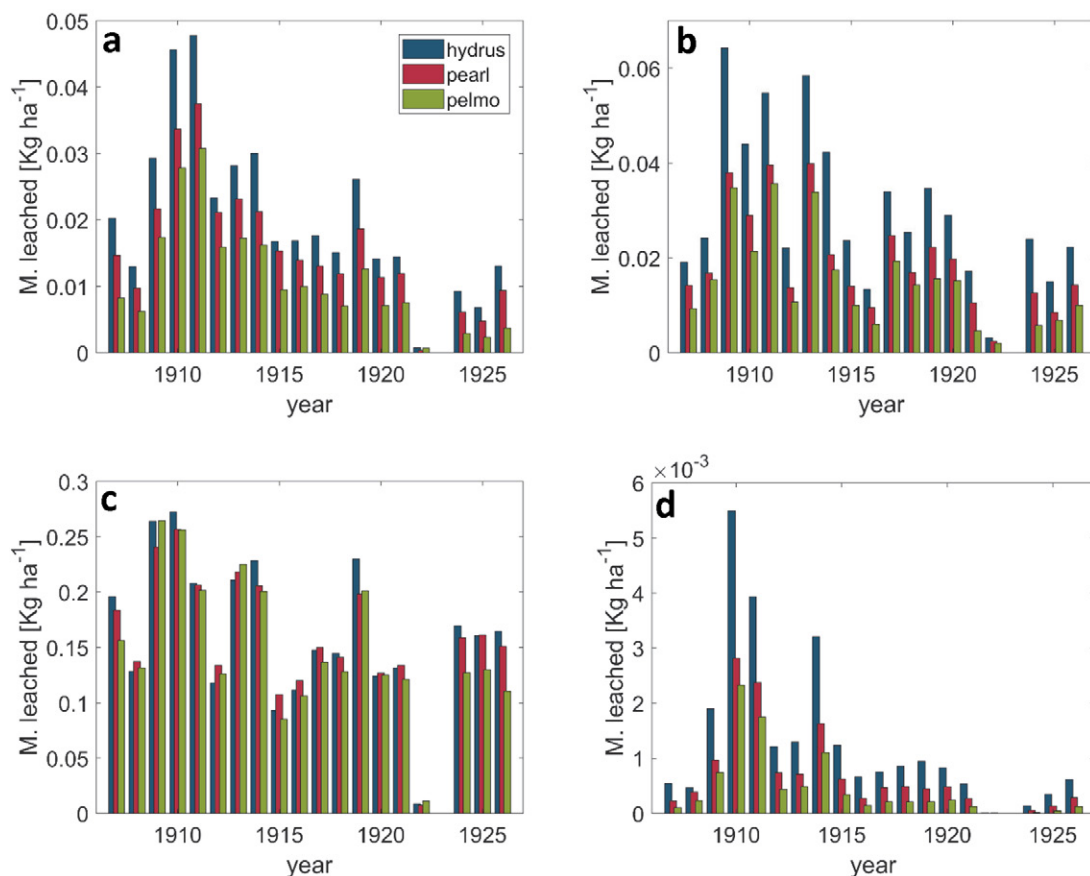


Fig. 2. Annual values of percolated mass ($M.$) as predicted by the three models for (a) Substance A, (b) Substance B, (c) a metabolite of Substance C, and (d) Substance D for the Kremsmünster scenario.

This is attributed to the higher actual soil evaporation calculated by HYDRUS. Higher actual evaporation leads to a lower soil water content in the soil profile, especially in its upper part, and consequently less degradation (or transformation) of the pesticides due to the dependence of biodegradation on water content (Eq. [18]). More pesticide mass remains dissolved in the soil profile, leading to higher leaching concentrations.

The function that describes the water content dependency of degradation is not a linear function (Eq. [18]). It also depends on the soil hydraulic properties (water dynamics). To assess the role of these conceptual model differences, simulations were run without moisture-dependent degradation by setting parameter B in Eq. [18] equal to 0 in both HYDRUS and PEARL. Under that scenario, HYDRUS predictions followed those of PEARL closely but were consistently about 10 to 15% lower than PEARL due to the lower PW in HYDRUS (Fig. 3).

For Châteaudun, all models predict similar values of yearly ET_{act} and PW (Fig. 4). HYDRUS results, while in significantly better agreement with PEARL than for the Kremsmünster scenario, are again consistently higher in ET_{act} values and consistently lower in PW values than PEARL. Despite the much better agreement between HYDRUS and PEARL in water flow dynamics,

HYDRUS here again predicts higher values of PM than PEARL for all substances (Fig. 5), similar to the Kremsmünster scenario, due to the differences in soil moisture dependent degradation discussed above. The larger differences (despite nearly identical flow dynamics) are not surprising given the sensitivity of mass transport to the upper boundary condition and soil moisture and the highly variable transport dynamics.

In the Piacenza scenario, the climate forcing is different, yet the results of the model runs are consistent with those for Kremsmünster and Châteaudun: HYDRUS predicts higher values of ET_{act} and consequently lower values of PW (Fig. 6). For Substances B and D, HYDRUS predicts higher PM values than PEARL (Fig. 7), similarly to the Kremsmünster scenario. For Substances A and C, HYDRUS results fell mostly between the PEARL and PELMO predictions of pesticide leaching. Similar results were obtained for the remaining six FOCUS scenarios.

In pesticide leaching assessments according to FOCUS (2000) and FOCUS (2014), an important output variable is the amount of water and pesticide mass flux that percolates to below a specific depth. A comparison of the 80th percentile (PE_w) of the annual volume of water percolated below the 1-m depth (PW), measured across 20 simulation years, shows that PEARL results, in most

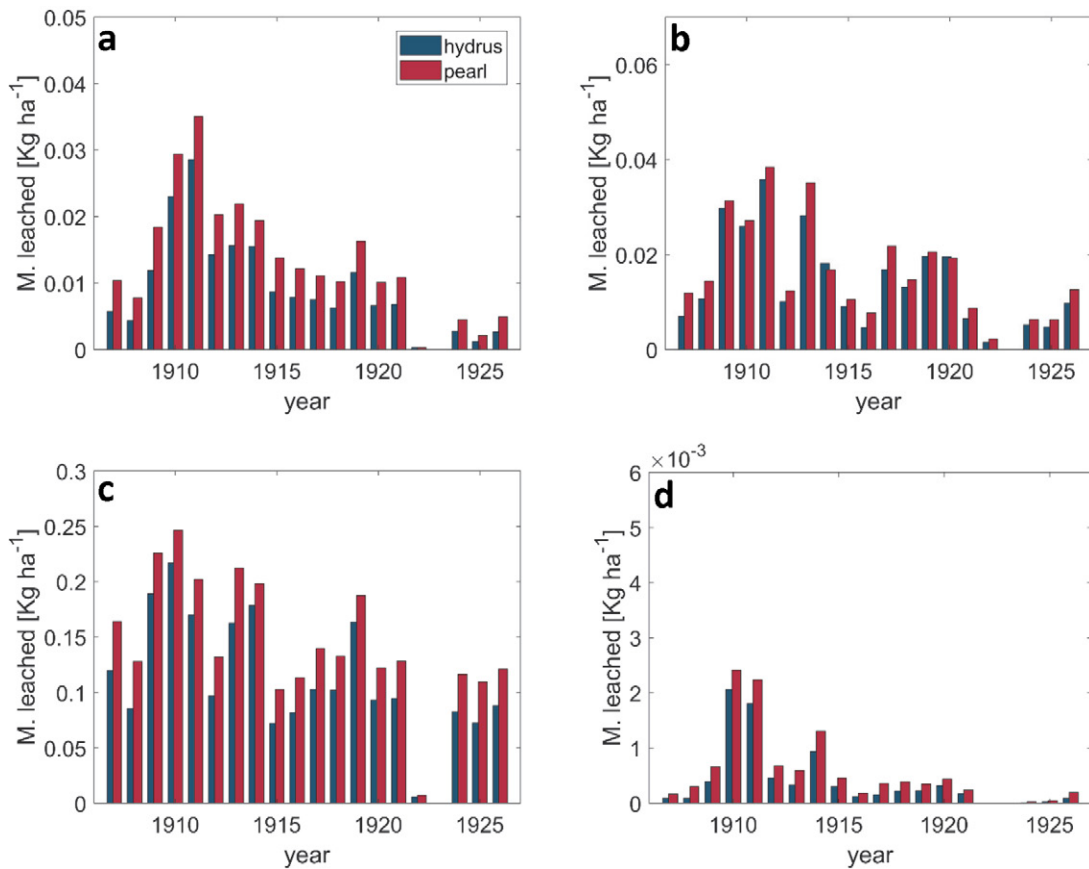


Fig. 3. Annual values of the mass percolated ($M.$) below 1 m as predicted by HYDRUS and PEARL assuming no water dependency of the degradation and transformation parameters for (a) Substance A, (b) Substance B, (c) a metabolite of Substance C, and (d) Substance D for the Kremsmünster scenario.

scenarios, agree somewhat better with HYDRUS results than with PELMO results (Fig. 8). The results agree best among the three models for scenarios using the free drainage and deep drainage boundary conditions and least for scenarios using variable pressure head boundary conditions (Fig. 8a). As described above, the variable pressure head boundary condition is not identical to the time-dependent groundwater position used in PEARL, resulting in increased values of PW for HYDRUS. The overall magnitude

of the differences between the 80th percentiles predicted by HYDRUS and PEARL is similar to that between PEARL and PELMO across all nine scenarios (Fig. 8b). The differences between HYDRUS and PEARL are smaller than the differences between PEARL and PELMO for seven scenarios. The root mean square difference between HYDRUS and PEARL ($PE_w^{HYDRUS} - PE_w^{PEARL}$) was 78 mm of water, whereas between PELMO and PEARL ($PE_w^{PELMO} - PE_w^{PEARL}$) it was 108 mm. Additionally,

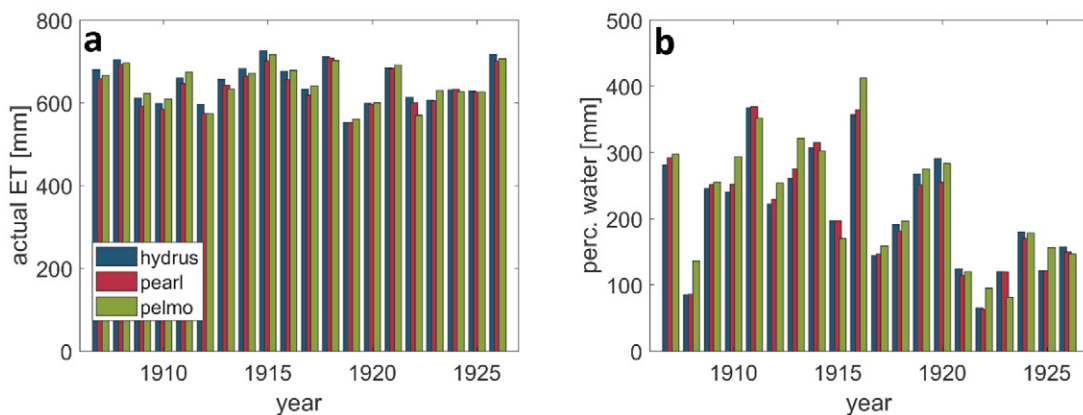


Fig. 4. (a) Annual actual evapotranspiration (ET_{act}) and (b) annual volumes of water percolated below the 1-m depth as predicted by the three numerical models for the Châteaudun scenario.

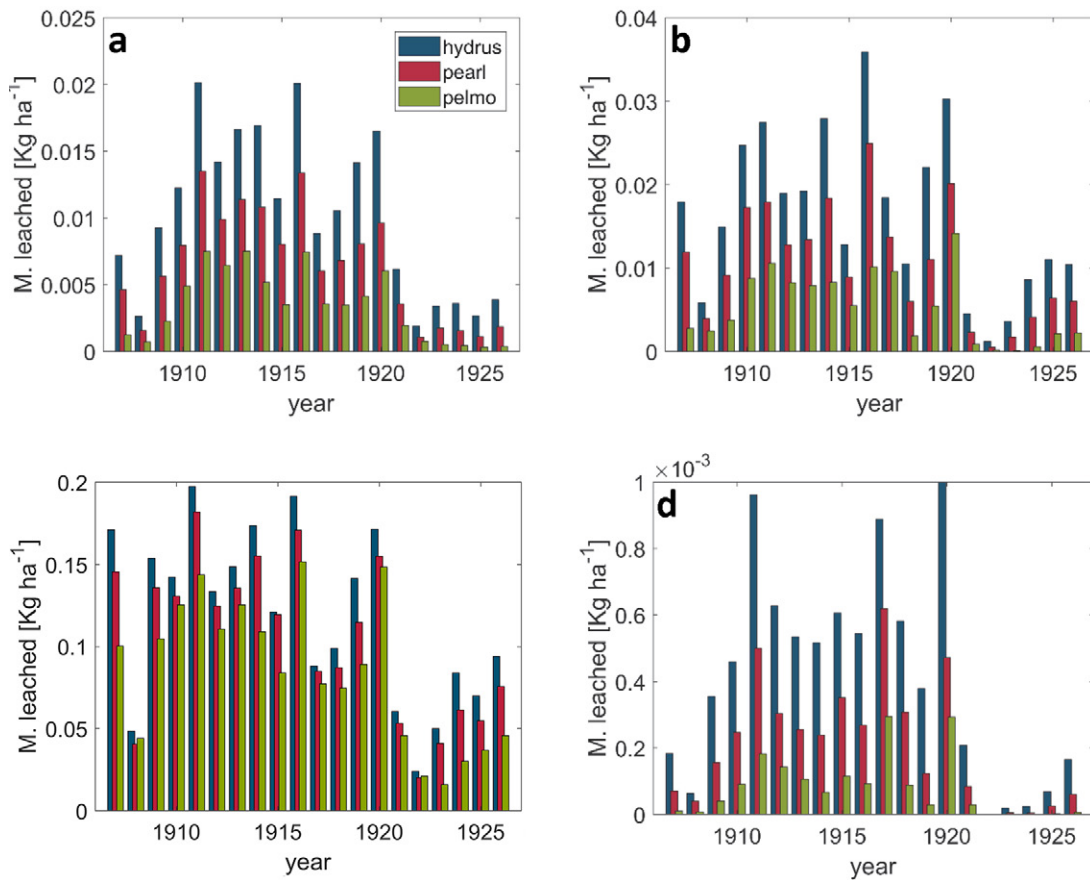


Fig. 5. Annual values of the mass percolated (M.) below 1 m as predicted by the three models for (a) Substance A, (b) Substance B, (c) a metabolite of Substance C, and (d) Substance D for the Châteaudun scenario.

we tested the null hypothesis that the two quantities ($PE_w^{HYDRUS} - PE_w^{PEARL}$ and $PE_w^{PELMO} - PE_w^{PEARL}$) are from populations with equal means. A two-sample *t*-test did not reject the null hypothesis at the 5% significance level ($p = 0.32$).

The works of both Scanlon et al. (2002) and Vanderborght et al. (2005) highlighted that the implementation of the upper boundary condition is very often associated with different predictions

for both water and solute transport. In model applications, it is therefore important that information exists to confirm the correct prediction of actual evaporation. For models based on the Richards equation, it further implies the need for accurate estimations near the soil surface, since actual evaporation is calculated as a function of the hydraulic conductivity curve. A better description of the soil hydraulic properties in the dry range is therefore critical, especially for applications in semiarid regions.

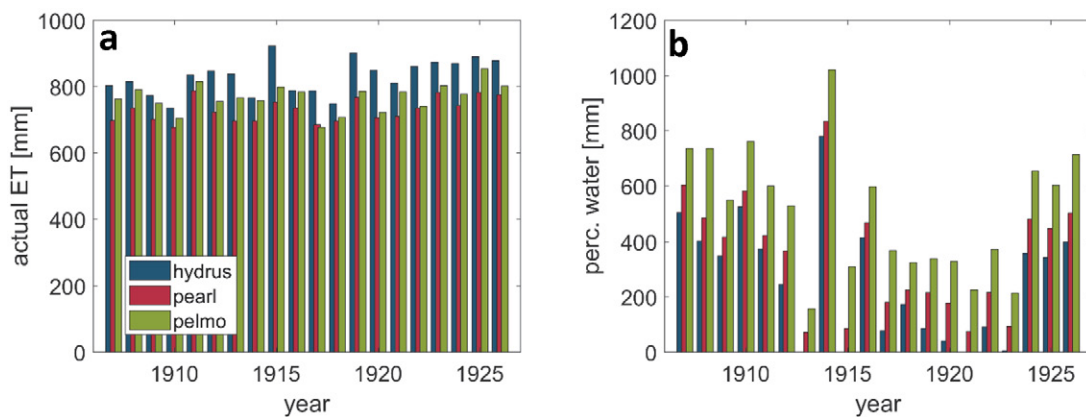


Fig. 6. (a) Annual actual evapotranspiration ET_{act} and (b) annual volumes of water percolated below the 1-m depth as predicted by the three numerical models for the Piacenza scenario.

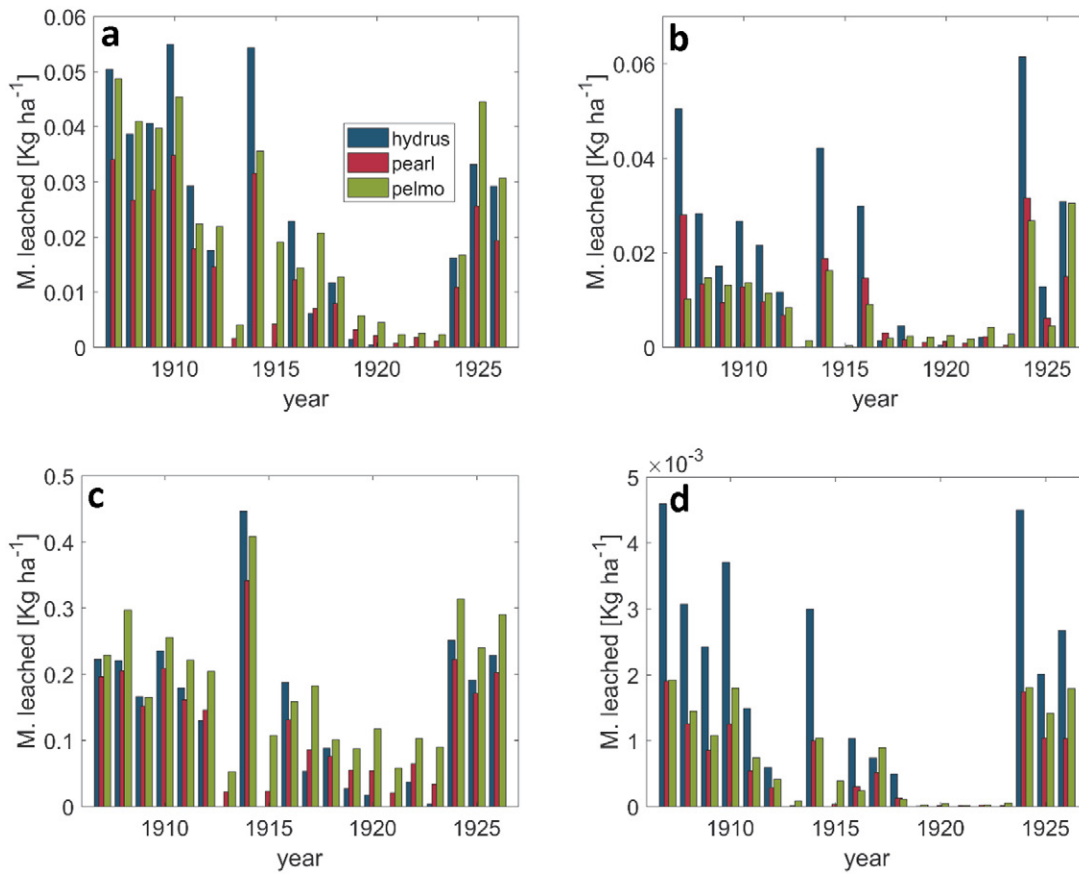


Fig. 7. Annual values of the mass percolated ($M.$) below 1 m as predicted by the three models for (a) Substance A, (b) Substance B, (c) a metabolite of Substance C, and (d) Substance D for the Piacenza scenario.

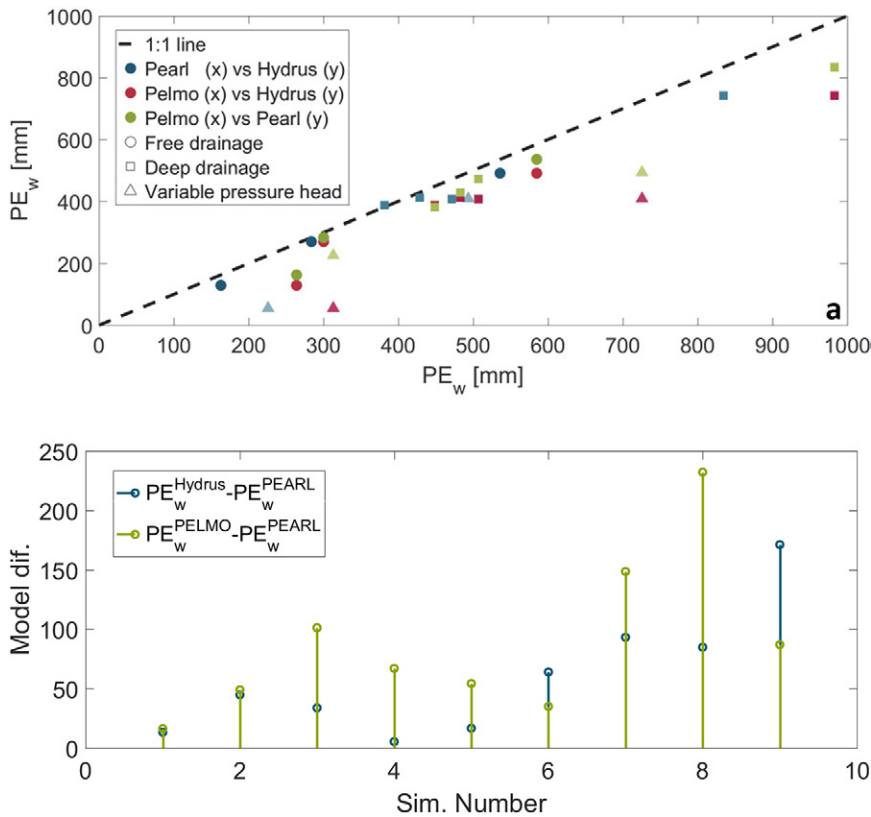


Fig. 8. (a) The 80th percentile of percolated water volumes (PE_w) below 1 m as predicted by the three models for the nine FOCUS (2000) scenarios, and (b) differences between PE_w^{HYDRUS} and PE_w^{PEARL} (blue) and between PE_w^{PELMO} and PE_w^{PEARL} (green).

The 80th percentiles of the annual mass flux during a 20-yr period, PEC_{gw} , vary across nearly four orders of magnitude for the four substances and nine scenarios (Fig. 9a). Given such a large range, the three models are in similarly good agreement with each other across different pesticide substances and scenarios, but particularly for those scenarios using a free drainage boundary, without any outliers (Fig. 9a). The differences in predicted percentiles between HYDRUS and PEARL are of the same magnitude as those between PEARL and PELMO (Fig. 9b). The root mean square difference of the logarithm of $(PEC_{gw}^{HYDRUS} - PEC_{gw}^{PEARL})$ was $0.98 \log_{10}(\mu\text{g L}^{-1})$, whereas the mean square difference of the logarithm of $(PEC_{gw}^{PELMO} - PEC_{gw}^{PEARL})$ was $1.02 \log_{10}(\mu\text{g L}^{-1})$. A two-sample *t*-test between the logarithms of $(PEC_{gw}^{HYDRUS} - PEC_{gw}^{PEARL})$ and $(PEC_{gw}^{PELMO} - PEC_{gw}^{PEARL})$, sampled for the nine scenarios and four pesticides (36 samples), reveals that the average difference between them is not significant ($p = 0.34$). As discussed above, HYDRUS consistently predicts higher PEC_{gw} relative to the other models while preserving the dynamic variability that is simulated by PEARL and PELMO.

Conclusion

The multidimensional HYDRUS (2D/3D) model was compared against two one-dimensional, standard EU regulatory models for the evaluation of water flow and pesticide transport in the

unsaturated zone for the nine different standard locations in the EU used by the FOCUS protocol and across four hypothetical pesticides with markedly different volatilization, sorption, and degradation behavior. An equivalent one-dimensional domain was set up in two dimensions with HYDRUS (2D/3D) to allow benchmark testing using the FOCUS protocol. The tests indicate that HYDRUS simulations provide results that are consistent with those obtained from the officially sanctioned models, PEARL or PELMO. Differences between HYDRUS and PEARL can be explained by differences in the treatment of boundary conditions and some differences in the formulation and parameterization of unsaturated zone flow. The magnitude of the differences between HYDRUS and PEARL is statistically not different from the magnitude of differences between other models within the regulatory suite of the FOCUS protocol. The results establish a strong point of reference for HYDRUS (2D/3D) to be used as an alternative to PEARL and PELMO. HYDRUS (2D/3D) would be most appropriate to use for regulatory assessments of pesticide fate and transport under conditions that are not adequately described by one-dimensional flow and transport, such as pesticide applications in micro-drip, micro-sprinkler, or in-furrow irrigation applications.

The comparison also revealed that different predictions of water dynamics (lower water leaching in the case of HYDRUS) may propagate inversely to pesticide transport (a higher mass leached

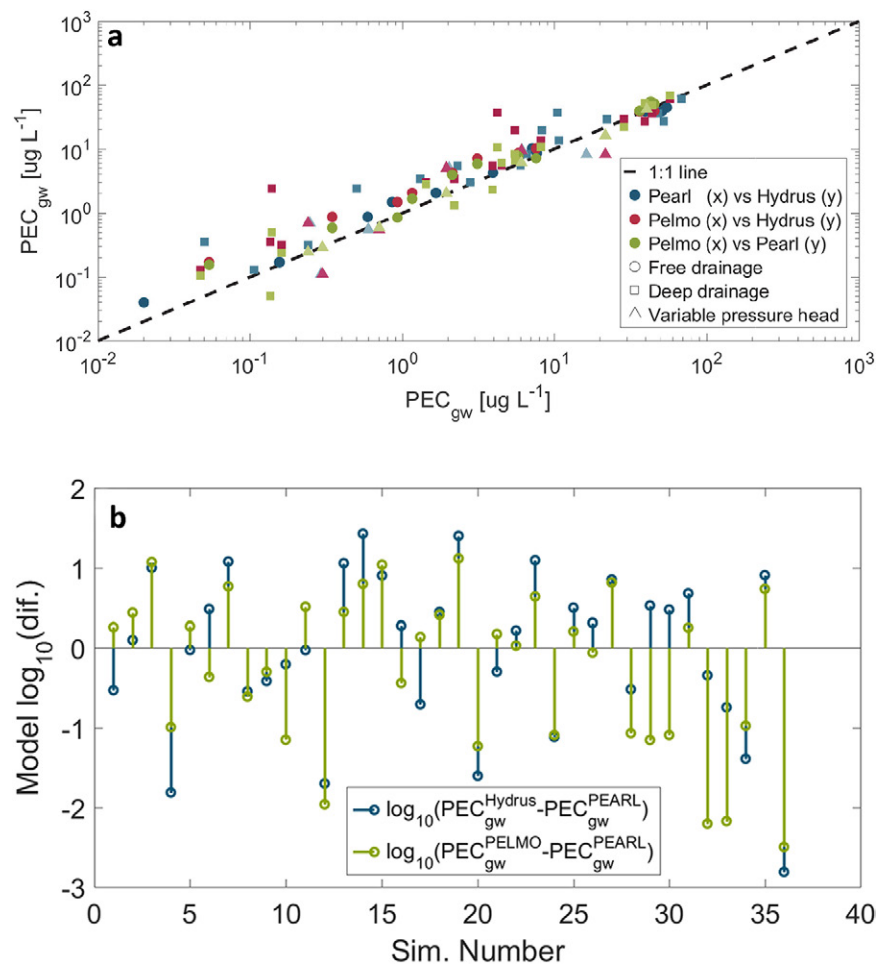


Fig. 9. (a) The 80th percentile of substance concentration (PEC_{gw}) at 1 m as predicted by the three models, the four dummy pesticides (A, B, a metabolite of C, and D), and the nine locations (total number of points: 108), and (b) the logarithms of the difference between PEC_{gw}^{HYDRUS} and PEC_{gw}^{PEARL} (blue) and between PEC_{gw}^{PELMO} and PEC_{gw}^{PEARL} (green).

in the case of HYDRUS). The prediction of relative drier soil near the soil surface in the case of HYDRUS resulted in long-term systematic differences in pesticide transport. This is due to interconnections between the two processes (water flow and pesticide transport). The interaction between processes like that are important and should be always taken into account in evaluating hydrological model predictions.

Acknowledgments

This study was financially supported by the Bayer AG Project "Development of FOCUS groundwater scenarios for multidimensional modeling of water flow and solute transport with HYDRUS 2D/3D." The opinions and findings expressed in this paper are solely those of the authors and have not been subject to review or approval by the funding agency. We acknowledge the thoughtful, critical comments of two anonymous VZJ reviewers, which helped to significantly improve this manuscript. HYDRUS input files for all FOCUS scenarios are available at <https://www.pc-progress.com/en/Default.aspx?h3d2-lib-focus>.

References

- Abdel-Nasser, G., A.M. Al-Turki, M.I. Al-Wabel, and M.H. El-Saeid. 2011. Behavior of atrazine and malathion pesticides in soil: Simulation of transport process using numerical and analytical models. *Res. J. Environ. Sci.* 5:221–235. doi:10.3923/rjes.2011.221.235
- Alaoui, A., P. Germann, N.J. Jarvis, and M. Acutis. 2003. Dual-porosity and kinematic wave approaches to assess the degree of preferential flow in an unsaturated soil. *Hydrol. Sci. J.* 48:455–472. doi:10.1623/hysj.48.3.455.45289
- Ashby, M., A.J. Dolman, P. Kabat, E.J. Moors, and M.J. Oginck-Hendriks. 1996. SWAP S version 1.0: Technical reference manual. Tech. Doc. 42. DLO Winand Staring Ctr., Wageningen, the Netherlands.
- Boesten, J.J.T.I., and L. Stroosnijder. 1986. Simple model for daily evaporation from fallow tilled soil under spring conditions in a temperate climate. *Neth. J. Agric. Sci.* 34:75–90.
- Boivin, A., J. Šimůnek, M. Schiavon, and M.Th. van Genuchten. 2006. Comparison of pesticide transport processes in three tile-drained field soils using HYDRUS-2D. *Vadose Zone J.* 5(3). doi:10.2136/vzj2005.0089
- Campbell, G.S. 1985. *Soil physics with Basic: Transport models for soil-plant systems*, Elsevier, New York.
- Carsel, R.F., J.C. Imhoff, P.R. Hummel, J.M. Cheplick, and A.S. Donigan, Jr. 1998. PRZM-3: A model for predicting pesticide and nitrogen fate in the crop root and unsaturated soil zones: Users manual for Release 3.0. USEPA, Natl. Exposure Res. Lab., Athens, GA.
- Carsel, R.F., J.C. Imhoff, P.R. Hummel, J.M. Cheplick, and A.S. Donigan, Jr. 2003. PRZM-3: A model for predicting pesticide and nitrogen fate in the crop root and unsaturated soil zones: User's manual for release 3.12. USEPA, Natl. Exposure Res. Lab., Athens, GA.
- Carsel, R.F., C.N. Smith, L.A. Mulkey, J.D. Dean, and P. Jowise. 1984. User's manual for the pesticide root zone model (PRZM), Release 1. EPA-600/3-84-109. USEPA, Environ. Res. Lab., Athens, GA.
- Chung, S.-O., and R. Horton. 1987. Soil heat and water flow with a partial surface mulch. *Water Resour. Res.* 23:2175–2186. doi:10.1029/WR023i012p02175
- Deb, S.K., P. Sharma, M. K. Shukla, J. Ashigh, and J. Šimůnek. 2016. Numerical evaluation of nitrate distributions in the onion root zone under conventional furrow fertigation. *J. Hydrol. Eng.* 21(2):05015026. doi:10.1061/(ASCE)HE.1943-5584.0001304
- Elmaloglou, S., E. Diamantopoulos, and N. Dercas. 2010. Comparing soil moisture under trickle irrigation modeled as a point and line source. *Agric. Water Manage.* 97:426–432. doi:10.1016/j.agwat.2009.11.003
- Estes, T.L., N. Pai, and M.F. Winchell. 2016. Comparison of predicted pesticide concentrations in groundwater from SCI-GROW and PRZM-GW models with historical monitoring data. *Pest Manage. Sci.* 72:1187–1201. doi:10.1002/ps.4097
- European Food Safety Authority. 2008. Scientific Opinion of the Panel on Plant Protection Products and their Residues on a request from EFSA related to the default Q10 value used to describe the temperature effect on transformation rates of pesticides in soil. *EFSA J.* 6:22. doi:10.2903/j.efsa.2008.622
- Feddes, R.A., P.J. Kowalik, and H. Zaradny. 1978. *Simulation of field water use and crop yield*. John Wiley & Sons, New York.
- Ferrari, F., M. Klein, E. Capri, and M. Trevisan. 2005. Prediction of pesticide volatilization with PELMO 3.31. *Chemosphere* 60:705–713. doi:10.1016/j.chemosphere.2005.01.043
- FOCUS. 2000. FOCUS groundwater scenarios in the EU review of active substances. EC Doc. Ref. Sanco/321/2000 rev.2. FOCUS Groundwater Scenarios Workgroup, European Soil Data Ctr., Brussels.
- FOCUS. 2014. Assessing potential for movement of active substances and their metabolites to ground water in the EU. EC Doc Ref Sanco/13144/2010 version 3. FOCUS Groundwater Scenarios Workgroup, European Soil Data Ctr., Brussels.
- Hoesel, W.V., A. Tiefenbacher, N. König, V.M. Dorn, J.F. Hagenguth, U. Prah, et al. 2017. Single and combined effects of pesticide seed dressings and herbicides on earthworms, soil microorganisms, and litter decomposition. *Front. Plant Sci.* 8:215. doi:10.3389/fpls.2017.00215
- Jarvis, N.J., L. Bergström, and P.E. Dik. 1991. Modelling water and solute movement in macroporous soil: II. Chloride leaching under non-steady flow. *J. Soil Sci.* 42:71–81. doi:10.1111/j.1365-2389.1991.tb00092.x
- Jury, W.A., W.F. Spencer, and W.J. Farmer. 1983. Behavior assessment model for trace organics in soil: I. Model description. *J. Environ. Qual.* 12:558–564. doi:10.2134/jeq1983.00472425001200040025x
- Klein, M. 1995. PELMO: Pesticide leaching model, user manual version 2.01. D57392. Fraunhofer-Institut für Umweltchemie und Ökotoxikologie, Schmallenberg, Germany.
- Köhne, J.M., S. Köhne, and J. Šimůnek. 2009a. A review of model applications for structured soils: A. Water flow and tracer transport. *J. Contam. Hydrol.* 104:4–35. doi:10.1016/j.jconhyd.2008.10.002
- Köhne, J.M., S. Köhne, and J. Šimůnek. 2009b. A review of model applications for structured soils: B. Pesticide transport. *J. Contam. Hydrol.* 104:36–60. doi:10.1016/j.jconhyd.2008.10.003
- Köhne, S., B. Lennartz, J.M. Köhne, and J. Šimůnek. 2006. Bromide transport at a tile drained field site: Experiment, and one- and two-dimensional equilibrium and non-equilibrium numerical modeling. *J. Hydrol.* 321:390–408. doi:10.1016/j.jhydrol.2005.08.010
- Kroes, J.G., J.C. van Dam, P. Groenendijk, R.F.A. Hendriks, and C.M.J. Jacobs. 2008. SWAP version 3.2. Theory description and user manual. Alterra Rep.1649. Alterra, Wageningen, the Netherlands.
- Larsbo, M., S. Roulier, F. Stenemo, R. Kasteel, and N.J. Jarvis. 2005. An improved dual-permeability model of water flow and solute transport in the vadose zone. *Vadose Zone J.* 4:398–406. doi:10.2136/vzj2004.0137
- Millington, R.J., and J.M. Quirk. 1961. Permeability of porous solids. *Trans. Faraday Soc.* 57:1200–1207. doi:10.1039/f96115701200
- Richards, L.A. 1931. Capillary conduction of liquids through porous mediums. *Physics* 1:318–333. doi:10.1063/1.1745010
- Scanlon, B.R., M. Christman, R.C. Reedy, I. Porro, J. Šimůnek, and G.N. Flerchinger. 2002. Intercode comparisons for simulating water balance of surficial sediments in semiarid regions. *Water Resour. Res.* 38(12):323. doi:10.1029/2001WR001233
- Šimůnek, J., M.Th. van Genuchten, and M. Šejna. 2012. The HYDRUS software package for simulating two- and three-dimensional movement of water, heat, and multiple solutes in variably-saturated porous media. Technical manual, Version 2.0. PC Progress, Prague, Czech Republic.
- Šimůnek, J., M.Th. van Genuchten, and M. Šejna. 2016. Recent developments and applications of the HYDRUS computer software packages. *Vadose Zone J.* 15(7). doi:10.2136/vzj2016.04.0033
- Tiktak, A., F. van den Berg, J.J.T.I. Boesten, M. Leistra, A.M.A. van der Linden, and D. van Kraalingen. 2000. Manual of FOCUS PEARL version 1.1.1. RIVM Rep. 711401008. Alterra Rep. 28. RIVM, Bilthoven, the Netherlands.
- van Dam, J.C., J. Huygen, J.G. Wesseling, R.A. Feddes, P. Kabat, P.E.V. van Walsum, et al. 1997. Theory of SWAP version 2.0: Simulation of water flow, solute transport and plant growth in the soil-water-atmosphere-plant environment. Tech. Doc. 45. DLO Winand Staring Ctr., Wageningen, the Netherlands.
- Vanderborght, J., R. Kasteel, M. Herbst, M. Javaux, D. Thiéry, M. Vanclooster, et al. 2005. A set of analytical benchmarks to test numerical models of flow and transport in soils. *Vadose Zone J.* 4:206–221. doi:10.2136/vzj2005.0206
- Vanderborght, J., and H. Vereecken. 2007. One-dimensional modeling of transport in soils with depth-dependent dispersion, sorption, and decay. *Vadose Zone J.* 6:140–148. doi:10.2136/vzj2006.0103
- van Genuchten, M.Th. 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.* 44:892–898. doi:10.2136/sssaj1980.03615995004400050002x
- Vereecken, H., A. Schnepf, J.W. Hopmans, M. Javaux, D. Or, T. Roose, et al. 2016. Modeling soil processes: Review, key challenges, and new perspectives. *Vadose Zone J.* 15(5). doi:10.2136/vzj2015.09.0131
- Walker, A. 1974. A simulation model for prediction of herbicide persistence. *J. Environ. Qual.* 3:396–401. doi:10.2134/jeq1974.00472425000300040021x