Single and dual-permeability models of chlorotoluron transport in the soil profile

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ABSTRACT

This study presents the transport of chlorotoluron in the soil profile under field conditions. The herbicide Syncuran was applied on a plot (4 m²) using an application rate of 2.5 kg/ha of active ingredient. Soil samples were taken after 119 days to study the residual chlorotoluron distribution in the soil profile. The single and dual-permeability models in HYDRUS-1D (Šimůnek et al. 2003) were used to simulate water movement and herbicide transport in the soil profile. Soil hydraulic properties and their variability were previously studied by Kutílek et al. (1989). The solute transport parameters, such as the adsorption isotherm and the degradation rate, were determined in the laboratory. Since the solute transport in the field was probably affected by preferential flow, the chlorotoluron distribution in the soil profile calculated using the single-permeability model had a different character than observed chlorotoluron concentrations. The chlorotoluron distribution within depth calculated using the dual-permeability model was closer to the observed behavior of chlorotoluron. While the herbicide did not reach a depth of 8 cm for the single-porosity system, in the case of the dual-permeability model the solute moved to the depth of 60 cm. The dual-permeability model significantly improved correspondence between calculated and observed herbicide concentrations.

Keywords: herbicide; chlorotoluron; solute transport; preferential flow; single pore system; dual-permeability; field and numerical studies

Soil and groundwater contamination by pesticides from agricultural activities is a worldwide environmental problem. Although pesticide and other contaminant concentrations can be monitored, such monitoring is quite expensive and time consuming. Various simulation models have been developed for assessment of groundwater vulnerability to contamination, resource management, and design of monitoring programs. The BPS (Kozák and Vacek 1996) and HYDRUS-1D (Šimůnek et al. 1998) models have been developed recently, among many others, to simulate water movement and solute transport in soils. The chlorotoluron transport in several soil types of the Czech Republic was studied experimentally and described with the BPS code (Kočárek et al. 2005). HYDRUS-1D was used to simulate chlorotoluron transport that was experimentally studied in chernozem (Kodešová et al. 2004). Both models can describe relatively well chlorotoluron behavior in soil profiles. However, simulated and observed herbicide distributions are often different, probably due to the effects of the preferential flow of water and solute in the soil profile and the spatial variability of transport parameters. In addition, some transport properties obtained under laboratory and field conditions may be quite different. Streck et al. (1995) presented apparent inconsistency between sorption isotherms determined from laboratory and field lysimeter experimental data. Poletika et al. (1995) used linear and nonlinear one- and two-stage sorption models to fit the sorption and desorption isotherms. Kamra et al. (2001) studied pesticides transport in small soil columns applying non-equilibrium two-region/mobile-immobile model. Flury et al. (1995) investigated preferential flow in the field. In this study herbicide was only partly sorbed by the soil matrix. A fraction of chemicals was transported with or without minor adsorption along cracks or fissures. Kočárek et al. (2005) observed chlorotoluron transport affected by preferential flow in 3 soil profiles from 5 studied soil types. Jorgensen et al. (2002) experimentally studied pesticides transport through preferential paths. For numerical simulation they used code FRAC3Dvs

(Therrien and Sudicky 1996) that simulated water and solute flow in fractured porous system. Gerke and van Genuchten (1993, 1996) proposed the dual-permeability model that solves flow and transport equations in both matrix and fracture pore systems. The MACRO model for simulation of water and solute transport in a dual-permeability system was developed by Jarvis (1994). MACRO was used for instance to simulate water and isoproturon behavior in a heavy clay soil by Besien et al. (1997). The MACRO model was also used for one scenario in the EU risk assessment program (FOCUS 2000).

Here we discuss the effect of preferential flow on chlorotoluron transport in the soil profile. Experimental field data presented in Kodešová et al. (2004) that involved the chlorotoluron transport in the soil profile were simulated using the modified HYDRUS-1D software package (Šimůnek et al. 1998, 2003). Preferential flow was evaluated by comparing results of the single-porosity and dual-permeability models (Gerke and van Genuchten 1993, 1996).

MATERIAL AND METHODS

The transport of chlorotoluron in the soil profile under field conditions was studied at the Tišice experimental field. The soil was defined as chernozem. Syncuran, containing 80% of active ingredients, was applied on a 4 m² plot on May 21st, 1997 at an application rate of 2.5 kg/ha of active ingredient. One liter of Syncuran solution (1.25 g/liter, e.g. 1 g/liter of chlorotoluron) was applied on the soil surface followed by irrigation with two liters of fresh water. Soil samples at depths of 0–2, 2–4, 4–6, 6–8, 8–10, 10–12, 12–14, 14–16, 16–18, and 18–20 cm were taken after 119 days to study the residual chlorotoluron distribution in the soil profile. The chlorotoluron concentrations in soil samples were determined in laboratory using standard laboratory procedures employing HPLC.

The chlorotoluron transport was numerically simulated using HYDRUS-1D (Šimůnek et al. 1998). Since the chlorotoluron was not studied under a depth of 20 cm, the soil profile was described as a one-dimensional flow region (60 cm) divided into two layers: 0–25 cm and 25–60 cm. The top boundary condition was defined by daily precipitation and estimated potential transpiration. Given the root zone depth of 20 cm, a Feddes model (Feddes et al. 1978) with parameters defined for wheat (winter barley) was applied to simulate the root water uptake. The bottom boundary condition was defined as a free drainage. The soil physical and hydraulic properties were studied before by Kutílek et al. (1989). The bulk densities

were 1.609 g/cm³ and 1.571 g/cm³ for the first and second layers, respectively.

Chlorotoluron transport in the soil profile was simulated using the single-porosity and dual-permeability models (Gerke and van Genuchten 1993, 1996) implemented in HYDRUS-1D. Review of models describing non-equilibrium and preferential flow and transport in the vadose zone has been given recently by Šimůnek et al. (2003). While the single-porosity model describes uniform flow in soil porous media, the dual-permeability model can represent a non-equilibrium/preferential flow in a complex system of soil aggregates (matrix) and intermediate spaces (fractures or macropores). In both studied cases is used Richards' equation describing the flow in a variably saturated rigid porous medium for one-dimensional isothermal Darcian flow. While the Richards' equation is solved for the entire flow domain for the single-porosity system, in the case of the dual-permeability model, it is applied separately to each of two pore regions – matrix and fracture domains. The soil hydraulic properties are described using van Genuchten (1980) equations for each domain. The analytical expressions for the soil water content retention curve, $\theta(h)$, and the hydraulic conductivity curve, $k(\theta)$, are:

$$\theta_e = \frac{\theta(h) - \theta_r}{\theta_s - \theta_r} = \frac{1}{\left(1 + |\alpha h|^n\right)^m} \ , \quad h < 0$$
$$\theta_e = 1, \quad h \geq 0$$
(1)

$$k(\theta) = K_s \cdot \theta_e^l \left[1 - (1 - \theta_e^{1/\mu})^\mu \right]^2, \quad h < 0$$
$$k(\theta) = K_s, \quad h \geq 0$$
(2)

where: θ_e is the effective soil water content (–), K_s is the saturated hydraulic conductivity (LT⁻¹), θ_r and θ_s are the residual and saturated soil water contents (L³L⁻³), respectively, l is the pore-connectivity parameter (–) ($l = 0.5$ in this case), and α (L⁻¹), n and m (= 1 – 1/n) are empirical parameters. The soil hydraulic parameters for the single-porosity system were for the depth from 0 to 25 cm as follows: $\alpha = 0.078$ cm⁻¹, $n = 1.29$, $\theta_r = 0.108$, $\theta_s = 0.406$, $K_s = 109$ cm/day; and from 25 to 60 cm as follows: $\alpha = 0.062$ cm⁻¹, $n = 1.33$, $\theta_r = 0.106$, $\theta_s = 0.414$, $K_s = 150$ cm/day. Assuming the ratio between the macropore and matrix regions equal to 0.1 parameters for the dual-permeability system for the depth from 0 to 25 cm were: $\alpha = 0.052$ and 0.07 cm⁻¹, $n = 1.22$ and 3, $\theta_r = 0.082$ and 0, $\theta_s = 0.398$ and 0.45, $K_s = 10$ and 1000 cm/day, and for the depth from 25 to 60 cm: $\alpha = 0.043$ and 0.06 cm⁻¹, $n = 1.27$ and 3, $\theta_r = 0.092$ and 0, $\theta_s = 0.407$ and 0.45, $K_s = 55$ and 1000 cm/day for the matrix and fracture pore systems, respectively. Soil water retention curves for both porosity systems are

shown in Figures 1 and 2. Following parameters are defined only for the dual-permeability model. Parameters describing aggregate shapes are the shape factor β (= 15 for spherical aggregates), the characteristic length of aggregate a (= 0.3 cm), and the dimensionless scaling factor γ_w (= 0.4). The interaction between the matrix and fracture regions is defined by the effective saturated hydraulic conductivity, K_a, equal to 0.01 cm/day. The mass exchange between the matrix and macropore region, Γ_w, is then calculated as follows:

$$\Gamma_w = \frac{\beta}{a^2} K_a \gamma_w \left(h_f - h_m \right) \tag{3}$$

where: h_f and h_m are pressure heads in the macropore and matrix domains, respectively.

Similarly the governing solute transport equation is solved for the entire flow domain (single-porosity system) and separately for both the macropore and matrix regions (dual-permeability system). Sorption parameters and degradation rates are assumed in this study to be the same in both regions. The adsorption isotherm relating adsorbed concentration of solute on soil particles (*s*) and solution concentration (*c*) is described by Freundlich equation:

$$s = k_F c^{\frac{1}{n_F}} \tag{4}$$

where: k_F ($L^{3/nF}M^{-1/nF}$) and n_F (–) are empirical coefficients. Parameters of the Freundlich adsorption isotherm were: k_F = 3.48 and 1.02, $1/n_F$ = 0.632 and 0.9 for the top and bottom layers, respectively. Herbicide degradation was assumed in both liquid and solid phases. Degradation rates were 0.02 per day and 0.002 per day in the top and bottom layers, respectively. Since the herbicide sorption and degradation are major processes, the molecular diffusion was neglected and longitudinal dispersivity was set to 1 cm.
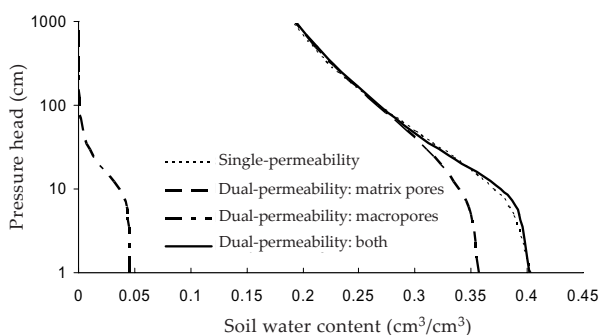
RESULTS AND DISCUSSION

Water regime

The water regime of the soil profile is documented in Figures 3 and 4. The cumulative actual surface water flux (evaporation – precipitation) at the top of the soil profile and the cumulative actual root water uptake are shown in Figure 3. The cumulative actual water outflow at the bottom of the soil profile is shown in Figure 4. The cumulative fluxes at the surface are 22.56 and 22.30 cm for the single- and dual-permeability models, respectively. The cumulative root water uptakes are 17.65 and 17.50 cm for the single- and dual-permeability models, respectively. The cumulative bottom fluxes are 8.54 and 9.14 cm for the single- and dual-permeability models, respectively. The fracture and matrix cumulative bottom fluxes for the dual-permeability model were 1.28 and 7.86 cm, respectively. While the surface flux and the root water uptake are driven mainly by the meteorological forcings, the bottom flux is determined mainly by the soil profile itself. The cumulative fluxes at surface and the cumulative root water are similar. The cumulative fluxes at the bottom are different. At the beginning of the simulation the bottom outflow is lower for the dual-permeability model than the single-permeability model. This is due to water being present initially mainly in the matrix pore system of the dual-permeability system and its lower hydraulic conductivity, compared to the matrix of the single-permeability system. Approximately in the middle of the simulated time period, the soil profile became almost saturated and considerable downward flow took place in both cases. Water was drained also through the macropores of the dual-permeability model and as a result, the cumulative outflow for the dual-permeability model is higher than the outflow for the single-permeability model.

Figure 1. Soil water retention curves for the depth from 0 to 25 cm for both single-permeability and dual-permeability models
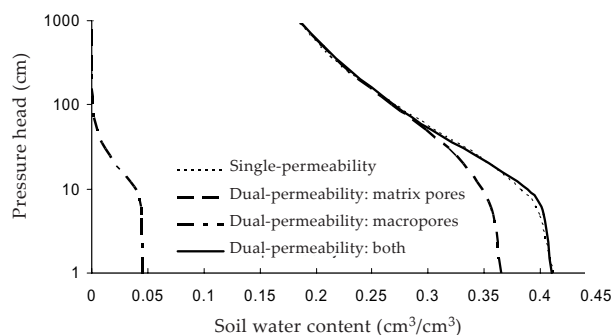

Figure 2. Soil water retention curves for the depth from 25 to 60 cm for both single-permeability and dual-permeability models
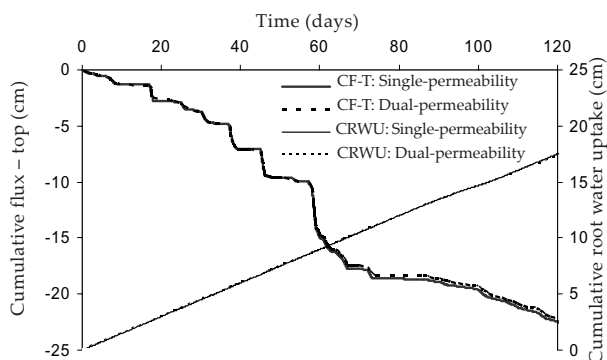
Figure 3. Cumulative actual water flux at the top of the soil profile (CF-T) and cumulative actual root water uptake (CRWU) after the herbicide application (+ upward flux, – downward flux)

Figure 4. Cumulative actual water flux at the bottom of the soil profile after the herbicide application (+ upward flux, – downward flux)

Solute transport

Simulated chlorotoluron concentrations in water in the soil profile 119 days after the application of Syncuran in the matrix pore systems of both models are shown in Figure 5. Simulated chlorotoluron concentrations in soil water for the fracture pore system of the dual-permeability model are shown in Figure 6. Solute concentrations in the matrix pore system in the top layer calculated using the single-permeability model are higher than concentrations calculated using the dual-permeability model. On the other hand, the herbicide is present also in the bottom layer for the dual-permeability model. The solute which was transported downwards mainly through the fracture pores was then redistributed into the matrix pores of the bottom layer. Interestingly, while there is a high concentration of solute in the matrix pore system at the depth of 0–8 cm, herbicide is no more present at this depth in the fracture pore system. The highest chlorotoluron concentrations in fracture pore water are in the bottom layer.

Observed concentrations in the soil profile were expressed as total amounts of solute per mass unit

of the soil. The simulated total amounts of solute (present in soil water and adsorbed on soil particles) per mass unit were therefore calculated to compare the measured and simulated chlorotoluron concentrations 119 days after the application (Figure 7). Simulated chlorotoluron concentrations in the soil profile for the single-porosity system are distributed very differently than the observed chlorotoluron concentrations. A single-porosity model did not predict presence of the herbicide below the depth of 8 cm, though the solute was observed at significant concentrations below this depth. The simulated chlorotoluron distribution in the soil profile obtained using the dual-permeability model is closer to the observed chlorotoluron distribution. However, concentrations at the top of the soil profile (0–2 cm) are lower than both observed and simulated concentrations using the single-permeability model and higher than observed concentrations at the depths of 12–20 cm. In addition, calculated chlorotoluron concentrations change abruptly at the boundary between two layers of the soil profile due to the different sorption properties of those layers. The sorption and degradation properties (depending on soil physical and
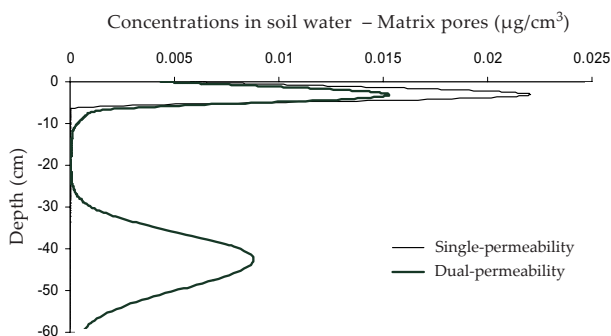

Figure 5. Simulated chlorotoluron concentrations in soil water in the matrix of the soil profile 119 days after the application of Syncuran for both single-permeability and dual-permeability models
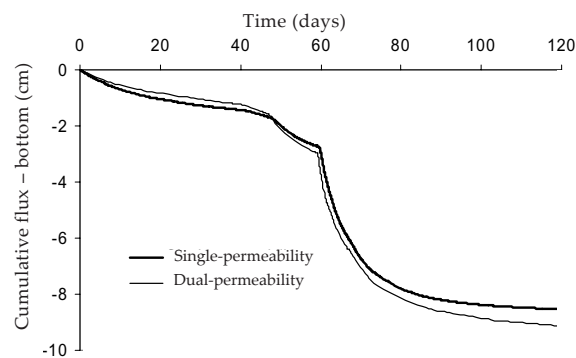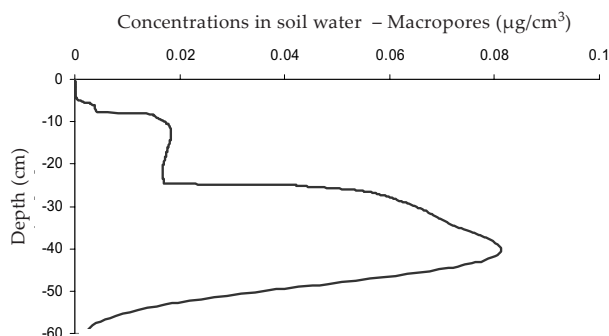

Figure 6. Simulated chlorotoluron concentrations in soil water in the macropores of the soil profile 119 days after the application of Syncuran for the dual-permeability model
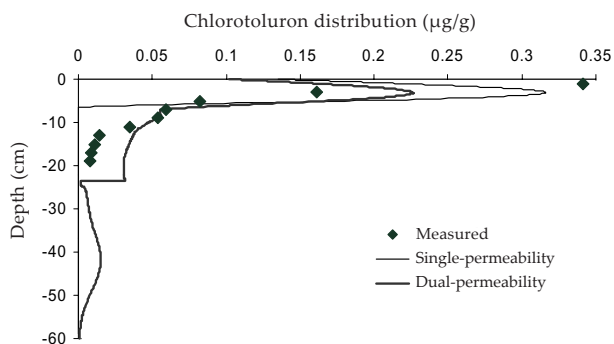
Figure 7. Measured and simulated residual chlorotoluron concentrations (expressed as total amount of solute per mass unit of soil) in the soil profile 119 days after the herbicide application
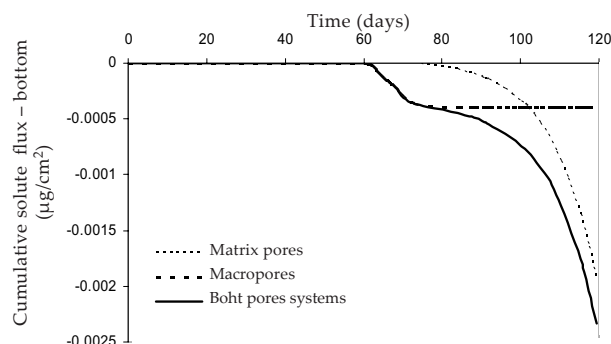

Figure 8. Simulated cumulative solute outflow at the bottom of the soil profile versus time from matrix pores, macropores and both pore systems for the dual-permeability model (+ upward flux, – downward flux)

chemical properties) usually gradually decrease with depth. Assuming such a gradient decrease of these two properties, simulated concentrations at depths of 12–25 cm would be probably lower and without a sudden change at the depth of 25 cm. Simulated and observed amounts of solute in the entire flow domain, CV, are similar: CV_{Single} = 2.294 μg/cm^2, CV_{Dual} = 2.393 μg/cm^2 (CV_{Matrix} = 2.390 μg/cm^2, $CV_{Fracture}$ = 0.003 μg/cm^2) and $CV_{Observed}$ = 2.49 μg/cm^2. Consideration of larger values of longitudinal dispersivity and molecular diffusion resulted in wider spread of herbicide in the soil profile (not shown). The resulting chlorotoluron concentrations in the soil profile however differed from the observed chlorotoluron concentrations even more than presented simulation results.

Solute moved to a depth of 60 cm in the dual-permeability system, compared to less than 10 cm for the single-porosity system. The cumulative solute outflow at the bottom of the soil profile simulated using the dual-permeability model is shown in Figure 8. Solute was drained initially only through the macropores and later from the matrix pore system as well. The macropore, matrix, and total cumulative solute fluxes were 0.0004, 0.0022 and 0.0026 μg/cm^2, respectively. Simulated and observed amounts of solute in the soil profile and the simulated total cumulative solute outflow showed that the herbicide was mostly degraded before reaching the bottom layer. Solute infiltrated mainly into the matrix pore system of the top layer that had higher sorption and degradation properties than the bottom layer. Solute bypassing the top layer through the macropores and then redistributed between macro- and matrix pores of the bottom layer with lower sorption and degradation properties was only slowly degraded and was more easily drained from the bottom layer. Description of

the bypass solute flow and leakage at the bottom of the soil profile into layers underneath, where sorption and degradation processes are mostly very low or even nonexistent, is especially important with respect to a ground water contamination. The dual-permeability model is a powerful tool that can provide an explanation of frequent groundwater contamination by pesticides in the Czech Republic (Kodeš 2003) and elsewhere, and for the estimation of contaminants leaching into the ground water.

Acknowledgement

REFERENCES

Besien T.J., Jarvis N.J., Williams R.J. (1997): Simulation of water movement and isoproturon behaviour in a heavy clay soil using the MACRO model. Hydrology and Earth System Sciences, *4*: 835–844.

Feddes R.A., Kowalik P.J., Zaradny H. (1978): Simulation of field water use and crop yield. John Wiley & Sons, New York, NY.

Flury M., Leuenberger J., Studer B., Flühler H. (1995): Transport of anions and herbicides in a loamy and sandy field soil. Water Resources Research, *31*: 823–835.

FOCUS (2000): FOCUS groundwater scenarios in the EU plant protection product review process. Report of the FOCUS Groundwater Scenarios Workgroup, EC Document Reference Sanco/321/2000, DG SANCO, EU Commission, Brussels.

Gerke H.H., van Genuchten M.Th. (1993): A dual-porosity model for simulating the preferential movement of

water and solutes in structured porous media. Water Resources Research, 29: 305–319.

Gerke H.H., van Genuchten M.Th. (1996): Macroscopic representation of structural geometry for simulating water and solute movement in dual-porosity media. Advances in Water Resources, 19: 343–357.

Jarvis N.J. (1994): The MACRO model. Technical description and sample simulation. Reports and dissertations 19. Department of Soil Science, Swedish University of Agricultural Science, Uppsala, Sweden.

Jorgensen P.R., Hoffmann M., Kistrup J.P., Bryde C. (2002): Preferential flow and pesticide transport in a clay-rich till: Field, laboratory, and modeling analysis. Water Resources Research, 38 (11).

Kamra S.K., Lennartz B., van Genuchten M.Th., Widmoser P. (2001): Evaluating non-equilibrium solute transport in small soil columns. Journal of Contaminant Hydrology, 48: 189–212.

Kočárek M., Kodešová R., Kozák J., Drábek O., Vacek O. (2005): Chlortoluron behaviour in five varying soil types. Plant, Soil and Environment, 51: 304–309.

Kodeš V. (2003): Occurrence of dangerous substances in groundwater of the Czech Republic. Acta Hydrologica Slovaca, 4: 183–189. (In Czech)

Kodešová R., Kozák J., Vacek O. (2004): Field and numerical study of chlorotoluron transport in the soil profile. Plant, Soil and Environment, 50: 333–338.

Kozák J., Vacek O. (1996): The mathematical model (BPS) for prediction of pesticide behaviour in soil. Rostlinná Výroba, 42: 69–76.

Kutílek M. et al. (1989): Structural assessment of the experimental field Tišice, Czech Republic. Department of Irrigation and Drainage, CTU, Prague.

Poletika N.N., Jury W.A., Yates M.V. (1995): Transport of bromide, simazine, and MS-2 coliphage in a lysimeter containing undisturbed, unsaturated soil. Water Resources Research, 31: 801–810.

Streck T., Poletika N.N., Jury W.A., Farmer W.J. (1995): Description of simazine transport with rate-limited, two-stage, linear and nonlinear sorption. Water Resources Research, 31: 811–822.

Šimůnek J., Jarvis N.J., van Genuchten M.Th., Gärdenäs A. (2003): Review and comparison of models for describing non-equilibrium and preferential flow and transport in the vadose zone. Journal of Hydrology, 272: 14–35.

Šimůnek J., Šejna M., van Genuchten M.Th. (1998): The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat and multiple solutes in variably-saturated media. Version 2.0. IGWMC-TPS-53. International Ground Water Modeling Center, Colorado. School of Mines, Golden, CO.

Therrien R., Sudicky E.A. (1996): Three-dimensional analysis of variably-saturated flow and solute transport in discretely-fractured porous media. Journal of Contaminant Hydrology, 23: 1–44.

van Genuchten M.Th. (1980): A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. Soil Science Society of American Journal, 44: 892–898.

ABSTRAKT

Modely jednoduché a duální propustnosti transportu chlortoluronu v půdním profilu

Transport chlortoluronu v půdním profilu byl studován v terénních podmínkách. Herbicid Syncuran byl aplikován na ploše 4 m^2, přičemž v dávce bylo 2,5 kg/ha účinné látky. Po 119 dnech byly odebrány půdní vzorky pro analýzu zbytkového obsahu chlortoluronu v půdním profilu. Pro simulaci pohybu vody a transportu herbicidu v půdním profilu byly použity modely jednoduché a duální propustnosti v HYDRUS-1D (Šimůnek et al. 2003). Hydraulické vlastnosti a jejich variabilitu studovali Kutílek et al. (1989). Transportní parametry jako adsorpční izoterma a degradační rychlost byly stanoveny v laboratoři. Rozdílný charakter rozdělení koncentrací pozorovaných a simulovaných modelem jednoduché propustnosti lze zdůvodnit preferenčním prouděním vody a roztoku. Průběh rozdělení koncentrací simulovaných modelem s duální propustností více odpovídá pozorovaným zjištěním. Zatímco se roztok v případě jednoduchého pórového systému nedostal dál než do hloubky 8 cm, v případě modelu duální propustnosti pronikl hlouběji pod 60 cm. Model duální propustnosti významně zlepšil popis pozorovaného rozdělení koncentrací.

Klíčová slova: herbicid; chlortoluron; transport roztoku; preferenční proudění; jednoduchý pórový systém; duální propustnost; terénní a numerická studie

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