Field and numerical study of chlorotoluron transport in the soil profile

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ABSTRACT

The transport of chlorotoluron in the soil profile under field conditions was studied. The herbicide Syncuran was applied on a four square meter plot using an application rate of 2.5 kg/ha active ingredient. Soil samples were taken after 119 days to study the residual chlorotoluron distribution in the soil profile. HYDRUS-1D (Šimůnek et al. 1998) was used to simulate water movement and herbicide transport in the soil profile. Soil hydraulic properties and their variability were studied previously by Kutílek et al. (1989). The solute transport parameters, like the adsorption isotherm and the degradation rate, were determined in the laboratory. The Freundlich and Langmuir equations were used to fit the experimental data points of the adsorption isotherm, and the affect of each type of adsorption isotherm equation on the solute transport was studied. The chlorotoluron concentrations in soil water tended to be higher for the simulation performed with the Freundlich isotherm then that of the model using the Langmuir isotherm. In both cases, the solution did not pass a depth of 8 cm. The simulated chlorotoluron concentrations in soil samples were higher then the observed concentrations when the chlorotoluron degradation was assumed to be in soil water only. Assumption of the solute degradation in both in the solid and the liquid phase significantly improved the accuracy of the solution. The different characters of the simulated and observed chlorotoluron distributions can probably be attributed to the preferential flow of water and solute in the soil profile and by variability of the transport parameters.

Keywords: herbicide; chlorotoluron; adsorption isotherm; degradation rate; solution transport; field and numerical studies

Soil and groundwater contamination from pesticides used in agriculture is a worldwide environmental problem. The situation is negatively influenced by increasing deterioration of soil physical conditions in intensive agriculture (Šantrůček and Svobodová 1992). Pesticide and other contaminant concentrations can be monitored. For instance, monitoring of the groundwater pollution in the Czech Republic was carried out by the Czech Hydrometeorological Institute (Kodeš 2003). However such monitoring is quite expensive and time consuming. Various simulation models have been developed for the assessment of groundwater vulnerability to contamination, resource management, and design of monitoring programs. Among other examples, the HYDRUS-1D and HYDRUS-2D software codes (Šimůnek et al. 1998, 1999) have been developed to simulate water movement and solute transport. The programs numerically solve the Richards' equation for saturated-unsaturated water flow and the convection-dispersion equation for solute and heat transport. The solute transport equations consider convective-dispersive transport in the liquid phase, convective-diffusive transport in the gaseous phase, non-linear equilibrium adsorption, and linear equilibrium reaction between the liquid and gaseous phases, zero-order production, and two first-order degradation reactions. The governing flow and transport equations are solved using the Galerkin-type linear finite element schemes.

In order to apply numerical models, the hydraulic properties of the soils and solute transport parameters must be determined. Numerous studies have been carried out to determine pesticide transport parameters, particularly organic carbon distribution and half life, or degradation rate, which describe mobility and persistence of pesticides, respectively. A comprehensive literary review of the subject has been published by Wauchope et al. (1992). More information is also available in accessible databases like the USDA database (http://www.arsusda.gov/acsl/ppdb.html). Indirect approaches have also been developed to estimate transport parameters. For instance, Kozák and Vacek (2000) presented an estimation of the distribution coefficient using the pedotransfer function.

In this study we present results of field experimentation and numerical simulations. The herbicide Syncuran was applied on a plot and residual chlorotoluron concentrations were studied in the soil profile after 119 days. Observed concentrations were compared with the numerically simulated results using HYDRUS-1D. Two equations (Freunlich

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and Langmuir) describing the adsorption isotherm obtained in the laboratory were used in numerical simulations. The influence of different equations on resulting herbicide concentrations in soil water is presented. The effect of the assumptions of herbicide degradation in water alone and in both solid and water phase is also discussed.

HYDRUS-1D (Šimůnek et al. 1998) was used to simulate water flow in unsaturated soil. The Richards' equation, in this case describing the flow in a variably saturated anisotropic homogeneous rigid porous medium for one-dimensional isothermal Darcian flow, can be written in the following simplified form:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[k\left(\frac{\partial h}{\partial z}+1\right)\right] \qquad (1)$$

where: z is the positive upward vertical coordinate (L), t is time (T), θ is the volumetric water content (L^3/L^3), h is the pressure head (L) and k is the unsaturated hydraulic conductivity function (L/T).

In this work, the van Genuchten (1980) expressions for the soil water content retention curve, $\theta(h)$, and the hydraulic conductivity curve, $k(\theta)$, are used:

$$\theta_e = \frac{\theta(h)-\theta_r}{\theta_s-\theta_r} = \frac{1}{\left(1+|\alpha h|^n\right)^m}, \quad h<0 \qquad (2)$$
$$\theta_e = 1, \quad h \geq 0$$

$$k(\theta) = K_s\, \theta_e^l \left[1-(1-\theta_e^{1/m})^m\right]^2, \quad h<0 \qquad (3)$$
$$k(\theta) = K_s, \quad h \geq 0$$

where: θ_e is the effective soil water content (–), K_s is the saturated hydraulic conductivity (L/T), θ_r and θ_s are the residual and saturated soil water contents (L^3/L^3), respectively, l is the pore-connectivity parameter (–) (l = 0.5 in this case), and α (per L), n and m (= 1 – 1/n) are empirical parameters.

Assuming that solute exists in liquid and solid (not in gaseous phase) and that the solute degrades in water and solid, the one-dimensional solute transport is described by the following simplified partial differential equation:

$$\frac{\partial \theta c}{\partial t} + \frac{\partial \rho s}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z}\right) - \frac{\partial qc}{\partial z} - \mu_w \theta c - \mu_s \rho s \qquad (4)$$

where: c is the solution concentration (M/L^3), s is the adsorbed concentration (M/M), ρ is the bulk density (M/L^3), D is the dispersion coefficient (L^2/T), q is the volumetric flux (L^2/T), μ_w and μ_s are the degradation rates in water and solid, respectively (per T).

The model assumes equilibrium interaction between the solution (c) and adsorbed concentration of solute on soil particles (s). The adsorption isotherm relating s and c is described by a generalized non-linear equation of the form:

$$s = \frac{k_s c^\beta}{1+\eta c} \qquad (5)$$

where: k_s (L^3/M), β (–) and η (L^3/M) are empirical coefficients. The Freundlich, Langmuir and linear adsorption equations are special cases of the equation (5). When $\beta = 1$, equation (5) becomes the Langumuir equation, when $\eta = 0$, equation (5) becomes the Freundlich equation, and when $\beta = 1$ and $\eta = 0$, equation (5) leads to a linear adsorption isotherm.

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 an 80% concentration of active ingredients, was applied on a 4 m^2 plot on May 21, 1997 at an application rate of 2.5 kg/ha of active ingredient. One liter of Syncuran solution (1.25 g/l, e.g. 1 g/l of chlorotoluron) was applied on the soil surface followed by irrigation with two liters of fresh water. Soil samples at depths 0–2, 2–4, 4–6, 6–8, 8–10, 10–12, 12–14, 14–16, 16–18, 18–20, 20–25, 25–30, 30–35, 35–40, 40–45, 45–50, 50–60, 60–70, 70–80, 80–90 and 90–100 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 the laboratory using standard laboratory procedures utilizing HPLC.

The chlorotoluron transport was numerically simulated using HYDRUS-1D. Since the chlorotoluron was not detected below a depth of 20 cm, the soil profile was described as a one-dimensional flow region (60 cm) divided into two layers: 0–25 and 25–60 cm. The top boundary conditions were defined by daily precipitation and estimated potential transpiration. Given the root zone depth of 20 cm, a Feddes model with parameters defined for wheat (winter barley) was applied to simulate the root water uptake. The soil physical and hydraulic properties were studied before by Kutílek et al. (1989). The bulk densities were 1.609 and 1.571 g/cm^3 for the first and second layers, respectively. The parameters of the van Genuchten functions are shown in Table 1.

Table 1. Parameters of the van Genuchten functions for the soil water retention and hydraulic conductivity curves

Layers (cm) cm	Hydraulic parameters				
	α (per cm)	n	θ_r (cm^3/cm^3)	θ_s (cm^3/cm^3)	K_s (cm/day)
0–25	0.052	1.22	0.082	0.398	52
25–60	0.043	1.27	0.092	0.407	186

Table 2. Parameters of the adsorption isotherms

	k_s (cm^3/g)	β (–)	η (cm^3/g)
Freundlich isotherm	3.4848	0.6319	0
Langmuir isotherm	9.2982	1	0.932

The parameters of the adsorption isotherm were not determined for this particular soil. Therefore the parameters obtained for another chernozem were used. Data points of the adsorption isotherm obtained in the laboratory were fitted with the Freundlich and Langmuir equations. The resulting parameters are shown in Table 2.

The persistence of chlorotoluron was studied in the laboratory, where the tests were performed under differing temperatures and soil water content conditions. HYDRUS-1D allows for simulating temperature dependence of transport parameters. In this study, however, the mean value of the degradation rate was used. The degradation of the herbicides is usually assumed to take place only in water, therefore the values μ_w = 0.02/day and μ_s = 0/day were applied.

RESULTS AND DISCUSSION

Water regime

The water regime in the soil profile is documented in Figures 1–4. Water inflow at the top of the soil profile is shown in Figure 1. Simulated root water uptake and water outflow at the bottom of the soil profile is shown in Figure 2. Simulated soil water content and pressure head distributions in the soil profile are shown in Figures 3 and 4, respectively. Numerical simulation was performed from April 1, 1997 to reach a realistic pressure head distribution when the herbicide was applied (May 21, 1997). However, all data and results are presented with respect to the day of the Syncuran application, e.g. time = 0 is on May 21, 1997. During the first half of

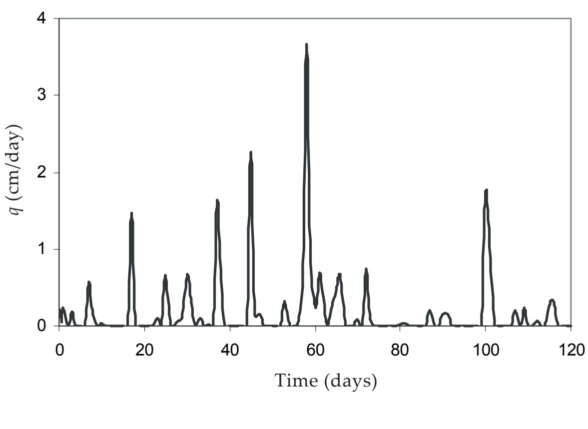

Figure 1. Water inflow (precipitation) at the top of the soil profile in time (time = 0 – day of Syncuran application)

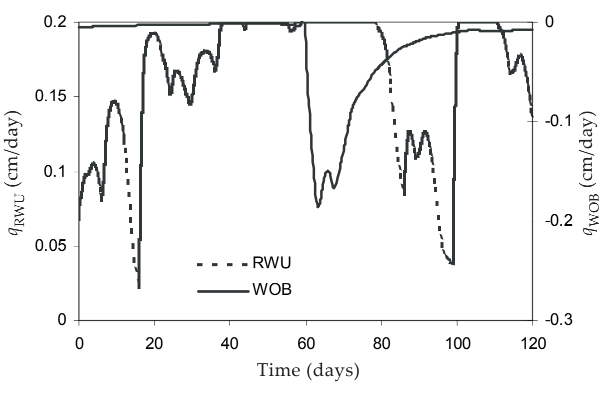

Figure 2. Simulated root water uptake (RWU) and water outflow at the bottom (WOB) in time (time = 0 – day of Syncuran application)

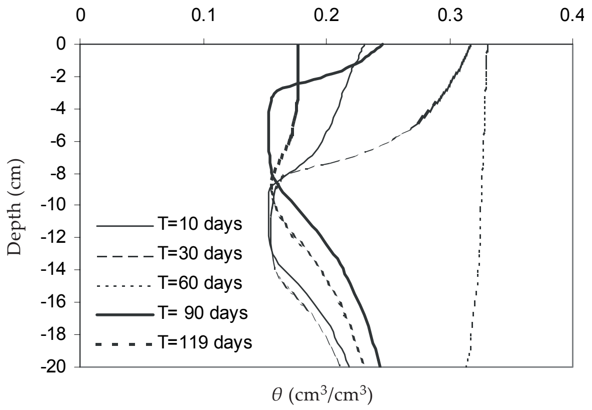

Figure 3. Simulated soil water content distribution in the soil profile 10, 30, 60, 90, 119 days after the application of Syncuran

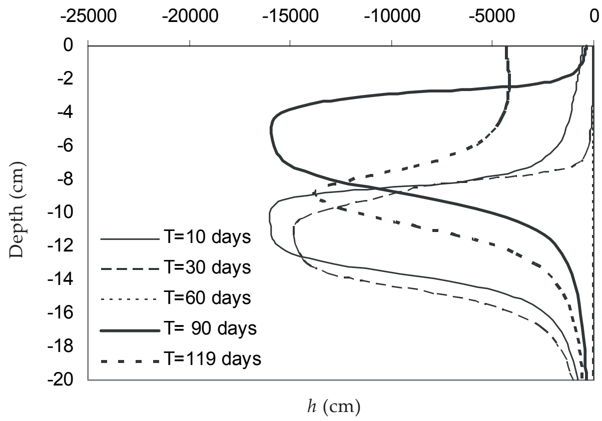

Figure 4. Simulated pressure head distribution in the soil profile 10, 30, 60, 90, 119 days after the application of Syncuran

the simulated period, water infiltrated at the top of the profile was mostly discharged from the soil profile by root water uptake. Approximately in the middle of that period, the soil profile became significantly saturated and considerable downward flow took place. After that the water infiltration on the top and root water uptake were again major processes.

Solute transport

First, the effect was studied of the different adsorption equations used for fitting of the measured data set on the solute transport. The resulting chlortoluron concentrations in soil water in the soil profile 10, 30, 60, 90 and 119 days after the application of Syncuran are shown in Figures 5 and 6 for Freundlich and Langmuir isotherms, respectively. The concentrations simulated with the Freundlich isotherm tend to be higher then those with the Langmuir isotherm. In both cases, the herbicide was not present below the depth of 8 cm. The concentrations at different time levels demonstrate that the solute was transported to depth mainly when the soil profile became saturated.

The observed concentrations in the soil profile were expressed as total amounts of solute present in the soil per mass unit. As shown in Figure 7, the simulated amounts of solute present in soil water and adsorbed on the soil particles per mass unit were calculated to compare the measured and simulated chlorotoluron concentrations 119 days after the application. The simulated concentrations are highly overestimated in both cases. The degradation of herbicides is usually assumed in water only. The degradation rate obtained in the laboratory was determined for total amount of the herbicide

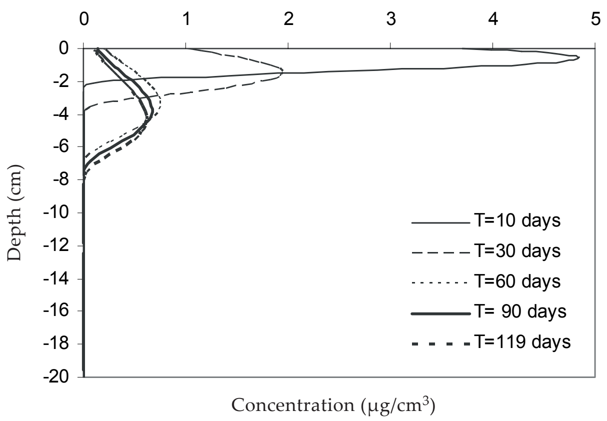

Figure 5. Simulated chlorotoluron concentrations in soil water in the soil profile 10, 30, 60, 90, 119 days after the application of Syncuran-Freundlich isotherm

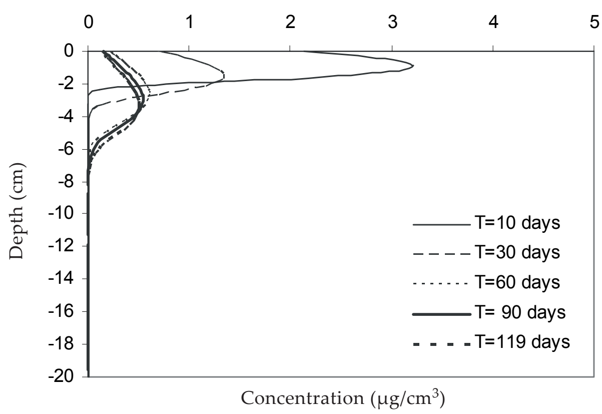

Figure 6. Simulated chlorotoluron concentrations in soil water in the soil profile 10, 30, 60, 90, 119 days after the application of Syncuran-Langmuir isotherm

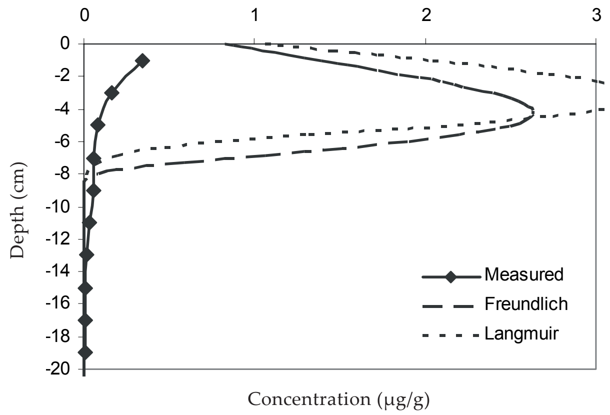

Figure 7. Measured and simulated residual chlorotoluron concentrations (expressed as total amount of solute per mass unit) in the soil profile 119 days after application, degradation rates μ_w = 0.02/day and μ_s = 0/day

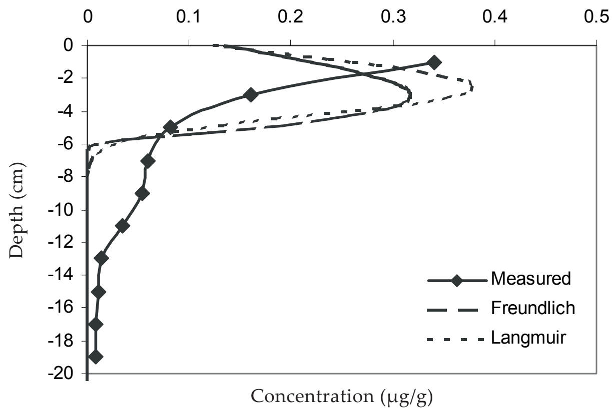

Figure 8. Measured and simulated residual chlorotoluron concentrations (expressed as total amount of solute per mass unit) in the soil profile 119 days after application, degradation rates μ_w = 0.02/day and μ_s = 0.02/day

in the soil. The real degradation rate in water is probably higher in this case, but the application of higher values did not significantly improve the solution (not shown). Therefore, the chlorotoluron degradation was assumed also in solid phase (μ_w = 0.02/day and μ_s = 0.02/day). The simulated chlorotoluron concentrations 119 days after the application are closer to measured values, as shown in Figure 8. Interestingly the simulated amount of solute in the entire flow domain, *CV*, is similar to the observed values ($CV_{Freundlich}$ = 22.79 μg/cm², $CV_{Langmuir}$ = 23.95 μg/cm² for μ_w = 0.02/day and μ_s = 0/day, $CV_{Freundlich}$ = 2.21 μg/cm², $CV_{Langmuir}$ = 2.36 μg/cm² for μ_w = 0.02/day and μ_s = 0.02/day, and *CV* = 2.49 μg/cm² observed). However, the observed chlorotoluron distribution in the soil profile has different character then simulated chlorotoluron distributions. The solute was observed below the depth of 8 cm. The highest chlorotoluron concentration is at the top and then decreases with the depth. The reason for this difference may be the water and solute preferential flow, since a part of the solute most likely penetrated quickly to depth immediately after application. The actual solute transport through the soil matrix was slower then the simulated one. In addition, the solute transport parameters depend on temperature and soil water conditions and may also be different compared to values obtained in the laboratory. This is especially important for the top layer, where the soil may become very dry and the biological degradation of herbicides is restricted. On the other hand, the herbicide may degrade on the top of the soil profile due to the solar radiation. To study these effects further, solute concentrations would have to be investigated with a high sampling frequency immediately after the solute application in the field. Dual-porosity and dual-permeability models in HYDRUS-1D may be used to numerically study the preferential flow problem. No recommendation can be made for the application of the different adsorption isotherms at this time. The proper definition of herbicide degradation should also be studied further.

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ABSTRAKT

Terénní a numerická studie transportu chlorotoluronu v půdním profilu

Transport chlorotoluronu v půdním profilu byl studován v terénních podmínkách. Herbicid Syncuran byl aplikován na ploše 4 m^2, v dávce byly 2,5 kg/ha účinné látky. Po 119 dnech byly odebrány půdní vzorky pro analýzu zbytkového obsahu chlorotoluronu v půdním profilu. Pro simulaci pohybu vody a transport herbicidu v půdním profilu byl použit HYDRUS-1D (Šimůnek a kol. 1998). Hydraulické vlastnosti a jejich variabilitu studovali již dříve Kutílek a kol. (1989). Transportní parametry jako adsorpční izoterma a degradační rychlost byly stanoveny v laboratoři. Pro proložení experimentálních bodů adsorpční izotermy byly použity rovnice Freundlichova a Langmuirova. Byl studován vliv rozdílných typů rovnic adsorpčních izoterm na transport rozpuštěné látky. Koncentrace chlorotoluronu v půdní vodě jsou vyšší pro simulaci s Freundlichovou izotermou než pro simulaci s Langmuirovou izotermou. Roztok se v obou případech nedostal dál než do hloubky 8 cm. Když byla uvažována degradace chlorotoluronu pouze v půdní vodě, simulované koncentrace chlorotoluronu v půdních vzorcích byly vyšší než pozorované koncentrace. Předpoklad, že degradace probíhá i na pevné fázi, výrazně zlepšil řešení. Rozdílný charakter simulovaných a pozorovaných rozdělení koncentrací lze zdůvodnit preferenčním prouděním vody a roztoku a variabilitou transportních parametrů.

Klíčová slova: herbicid; chlorotoluron; adsorpční izoterma; degradační rychlost; transport roztoku; terénní a numerická studie

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