Chlortoluron behavior in five different soil types

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ABSTRACT

Chlortoluron transport was studied in five different soil types and under varying climatic conditions. The chlortoluron mobility in the monitored soils increases as follows: Albic Luvisol = Haplic Luvisol < Haplic Cambisol < Haplic Stagnosol < Greyic Phaozem. Significantly high concentrations in the top layer of Haplic Stagnosol were observed due to the high presence of coarse gravel (30–40%) and flow profile reduction up to 60%. The content of remaining chlortoluron in the soil profile corresponds to the herbicide mobility. The percentages of remaining chlortoluron were 46.1% in Albic Luvisol, 54.6% in Haplic Luvisol, 65.0% in Haplic Cambisol, 69.6% in Haplic Stagnosol and 102.9% in Greyic Phaozem. The highest herbicide degradations were at the locations with lower observed mobility and herbicide present mainly in the top layer. Occurrence of the remaining chlortoluron percentage in Greyic Phaozem higher than 100% was caused mainly by the herbicide transport through the preferential paths and restricted degradation in subsurface layers. Variability of chlortoluron distributions in the soil profiles observed at the three positions of the same location occurred due to the heterogeneity of the soil profile and an uneven distribution of chlortoluron on the soil surface. The BPS mathematical model (Kozák and Vacek 1996) connected with the soil database (Kozák et al. 1996) was used to simulate chlortoluron transport. The simulated chlortoluron concentrations follow approximately the measured data except for Greyic Phaozem, where a preferential flow highly influenced solution transport. The BPS model with the soil database can be used for estimation of the chlortoluron transport.

Keywords: pesticides; chlortoluron; degradation; solution transport; field and numerical study

Many studies have been devoted to the monitoring of pesticide contamination of drainage water. The existing literature however provides only a little information about actual behavior of the pesticides in the soil profile under field conditions. The pesticides transport in the field was studied for instance by Stolpe et al. (1998), Rochaud et al. (2000), Schiavon et al. (2000) and Renaud et al. (2004).

Chlortoluron, tested in this study, is a widely used herbicide that prevents weeds growing in productions of cereals and poppy. Zander et al. (1999) proved the presence of chlortoluron in 15% from the total of 2403 tested groundwater samples in western Germany. Chlortoluron concentrations in 7% of samples were higher than 0.1 μg/l, i.e. they were higher than the maximum limit value of the drinking water standard.

Chlortoluron behavior studies, which were done in laboratory as well as in field, were concentrated mainly on the sorption and degradation processes. Degree of pesticide losses varied from soil to soil, depending on structural development and the organic carbon content. Pesticide degradation experiments on disturbed and undisturbed soil samples showed that the rapid decline of leached loads with time was faster than could be explained by degradation alone (Renaud et al. 2004). Chlortoluron degradation starts with two ways. It is namely chlorination and hydroxylation of the aromatic ring followed by consecutive chlorination reaction after almost two weeks of ring opening and partial mineralization (Losito et al. 2000).

Rochaud et al. (2000) studied the pesticide degradation time on the plots that had not been previously treated with herbicides, and on the plots, which had been treated with the same herbicide annually during 12 years. In the plots treated for the first time with either diuron, chlortoluron or simazin, the half-lives of these herbicide in the 0–10 cm surface soil layer were 81, 64, and 59 days, respectively. In the plots treated with the same herbicide for 12 years, the corresponding half-lives were 37, 11, and 46 days. The accelerate biodegradation could reduce the weed control of diuron and chlortoluron. On the other hand, the accelerated biodegradation reduces concern about the possible accumulation of these herbicides in the soil.

Microorganisms are the most important for pesticide degradation in soil. The best results of degradation were obtained with *Bjenkardera adusta* and *Oxysporus* species that were the most

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efficient towards three substrates. After two weeks *Bjenkardera adusta* depleted chlortoluron 98%, diuron 92% and isoproturon 88% (Khadrani et al. 1999).

Various simulation models have been developed for assessment of groundwater vulnerability to contamination, resource management, and design of monitoring programs. The chlortoluron transport in several soil types of the Czech Republic was studied experimentally and described with the BPS code (Kočárek et al. 2004). HYDRUS-1D (Šimůnek et al. 1998) was used to simulate chlortoluron transport that was experimentally studied in chernozem (Kodešová et al. 2004 and 2005).

Here we present results of field and numerical studies at five location of the Czech Republic. Chlortoluron transport was studied in five different soil types and under different climatic conditions. The BPS mathematical model (Kozák and Vacek 1996) was employed to simulate herbicide transport.

MATERIAL AND METHODS

Experiments were carried out in Albic Luvisol (Hněvčeves), Haplic Luvisol (Kostelec nad Orlicí), Haplic Cambisol (Humpolec), Haplic Stagnosol (Vysoké nad Jizerou), Greyic Phaozem (Čáslav). One liter of water containing 1 g of chlortoluron was applied on experimental plots 2 × 2 m. Two liters of fresh water were used to wash down the herbicide of plants and ensure the solution inflow into the soil. Soil samples from layers 2 cm thick (to the total depth of 30 cm) were taken using the Eijkelkamp sampler at three positions of each experimental plot 35 days after the chlortoluron application. The cooling box was used to transport soil samples from the experimental field to the laboratory.

The soil samples were analyzed in the laboratory to determine chlortoluron distributions in the soil profiles. The soil samples were dried, grinded and sieved through the 1-mm sieve. The total amount of chlortoluron in each soil sample was determined in following way. 5 g of dry soil were placed into a centrifuge cuvette. 5 ml of methanol were added and the centrifuge cuvette was placed for 15 hours into the shaking apparatus. After that, the analyzed soil sample was centrifuged 30 minutes with 12 000 spins per minute. The chlortoluron concentration in the methanol extract was determined using the HPLC technology. The total amount of chlortoluron present in the soil sample was expressed as the total amount of solute per mass unit (μg/g). The average value from 3 samples for each layer was calculated.

The HPLC instrument was put together from various easily replaceable components. The pump Consta Metric 4100 (product of LDC Analytical Company) was equipped with additional pulse suppressor. Samples were inserted via automatic sampler Triatlon (Spark). The space (and time) between injection and chromatography column was minimized. The separation took place in the Nucleosil 120-5, C18 column, 125 × 4 mm (Watrex). To prolonged lifetime of this column was used the Guard column insert (10 × 4 mm) peak. Mobile phase was prepared by mixing 600 ml of methanol, 400 ml of redistilled water and 6 ml of NH_4OH. The flow rate of this mobile phase was kept at the level of 0.8 ml per minute. Detection of chlortoluron was performed online in UV region (310 nm) by means of UVD 200 detector (DeltaChrom). The signal from the detector was processed and stored by chromatographic software CSW 1.7 (DataApex). The analyses were run under stable laboratory conditions (temperature 20°C).

The BPS mathematical model (Kozák and Vacek 1996) was used to simulate herbicide transport in studied soil types. The daily precipitations were measured at each location. Evapotranspiration was estimated by the BPS model assuming minimum, maximum and average daily temperatures. The soil physical, hydraulic and chemical properties were studied for each location. However, the mean values of properties for each soil type stored in the soil database (Kozák et al. 1996) that is connected

Table 1. Physical and chemical properties of studied soil

Location	C.E.C. (mmol/ 100 g)	Ha (mmol/ 100 g)	BC (mmol/ 100 g)	BS (%)	pH (H_2O)	pH (KCl)	C_{org} (%)	A_{400}/A_{600}	Va (mmol/ 100 g)	$CaCO_3$ (%)	P (g/cm^2)
Albic Luvisol	15.54	4.00	11.54	74.26	6.3	5.5	1.10	4.43	0.17	0.1	1.47
Haplic Luvisol	13.74	6.50	13.50	52.69	5.6	5.0	1.30	5.21	0.18	0.1	1.58
Haplic Cambisol	14.38	7.52	7.20	49.97	6.6	6.0	1.65	5.33	0.24	0.1	1.39
Haplic Stagnosol	18.00	9.50	8.50	47.22	6.0	5.3	1.86	7.15	1.18	0.1	1.42
Greyic Phaozem	19.52	0.00	19.52	100.00	7.6	6.1	0.85	4.19	0.12	0.3	1.52

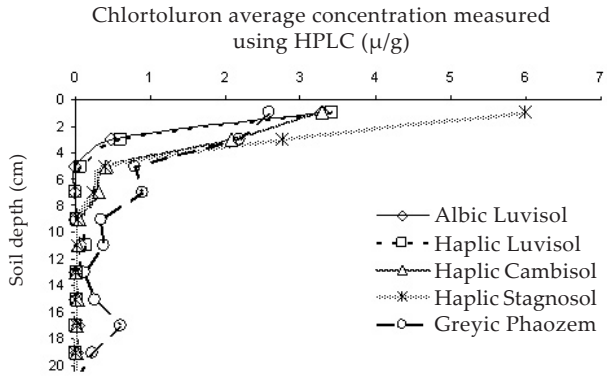

Figure 1. Measured average chlortoluron concentrations (expressed as total amount of solute per mass unit) in the soil profiles in studied soils

with BPS were applied to study ability of such inputs for general characterization of herbicide transport in specific soil type. The soil hydraulic properties, sorption and half-time degradation were estimated using the pedotransfer functions and rules (Kozák and Vacek 2000). Soil physical and chemical properties determined for each location and used as inputs into the BPS model are shown in Table 1.

RESULTS AND DISCUSION

Experimental data show differences between the pesticide transports in the different soil types and under varying climatic conditions (Figure 1). Chlortoluron mobility in the monitored soils increases as follows: Albic Luvisol = Haplic Luvisol < Haplic Cambisol < Haplic Stagnosol < Greyic Phaozem. The herbicide almost did not move in both Luvisols (Albic Luvisol and Haplic Luvisol). In the other three soil profiles, chlortoluron is not gradually distributed as would be expected, assuming a uniform water flow and solute transport in a rigid porous medium. The herbicide transport in those soil profiles was probably influenced by preferential flow that occurs due to the higher content of sand and gravel in Haplic Stagnosol (clay 5%, silt 69%, sand 26%, gravel 32%) and Haplic Cambisol (clay 5%, silt 49%, sand 46%, gravel 6%). In the case of Greyic Phaeozem, where the preferential flow highly influenced solution transport, the reason may be volume changes (clay 21%, silt 66%, sand 13%, gravel 0%) and influence of living organisms. The saturated hydraulic conductivities obtained in studied Greyic Phaeozem show the highest variability ($2.8.10^{-3}$ – $9.6.10^{-6}$ cm/s). Similarly, the higher mobility of chlortoluron, isoproturon and triasulfuron was observed by Walker et al. (2005) in the structured clay loam than in the unstructured sandy loam .The chlortoluron concentration in the top layer of Haplic Stagnosol is significantly higher than concentrations at the other locations. In this case, the high content of coarse gravel (30–40%) reduced flow profile up to 60% and as a result, experimental data actually represent accumulated chlortoluron in this reduced flow domain.

The total amounts of chlortoluron in the soil profile (0–30 cm) and the percentages of remaining chlortoluron from the theoretically applied dose were calculated using the average bulk density. Considering an impact of the gravel, the bulk densities in Haplic Stagnosol and Haplic Cambisol were multiplied by the ratio between the reduced and entire flow domain equal to 0.65 (Haplic Stagnosol) and 0.92 (Haplic Cambisol) to obtain chlortoluron balance for entire flow domain. The average total amounts of chlortoluron and percentages of remaining chlortoluron demonstrate different chlortoluron degradation rates in the monitored soil types (Albic Luvisol 11.52 mg/cm^2, 46.1%, Haplic Luvisol 13.65 mg/cm^2, 54.6%, Haplic Cambisol 17.66 mg/cm^2, 65.0%, Haplic Stagnosol 26.78 mg/cm^2, 69.6% and Greyic Phaozem 25.81 mg/cm^2, 102.9%). These results show that the highest herbicide degradations were at the locations with lower observed mobility and herbicide presence mainly in the top layer. Herbicide was more degraded at those locations because of the higher degradation rates in the surface soil layers. As was presented by Hamaker (1972), the degradation rates in the subsurface layers may differ significantly from those in the surface layers because of changes in soil conditions such as organic mater content, microbial activity, moisture content and temperature. The initial rapid degradation of the herbicides should be also assumed to be attributed to the substantial biological activity in the topsoil, where the herbicides are available to microbes before the first mayor rainfall (Sarmah et al. 2000). In addition, the herbicide at the surface may be degraded due to the solar radiation and volatilization. Interestingly, the percentage of remaining chlortoluron in Greyic Phaozem is

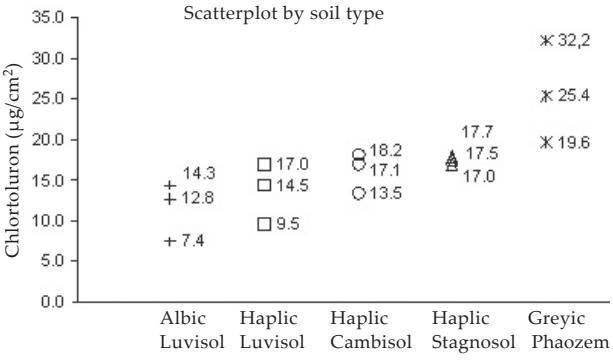

Figure 2. Total mass of the chlortoluron in the soil profile (μg/cm^2) 35 days after application in studied soils

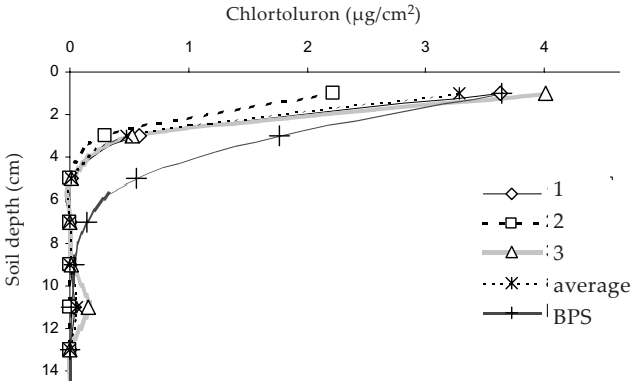

Figure 3. Measured and simulated chlortoluron concentrations (expressed as total amount of solute per mass unit) in the soil profile 35 days after application in Albic Luvisol: 1, 2 and 3 – measurement at 3 sampled positions, average – averages from this three measurements, BPS – predicted concentrations using the BPS model

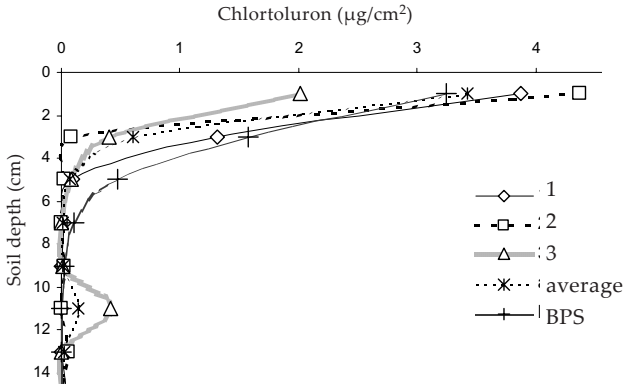

Figure 4. Measured and simulated chlortoluron concentrations (expressed as total amount of solute per mass unit) in the soil profile 35 days after application in Haplic Luvisol: 1, 2 and 3 – measurement at 3 sampled positions, average – averages from this three measurements, BPS – predicted concentrations using the BPS model

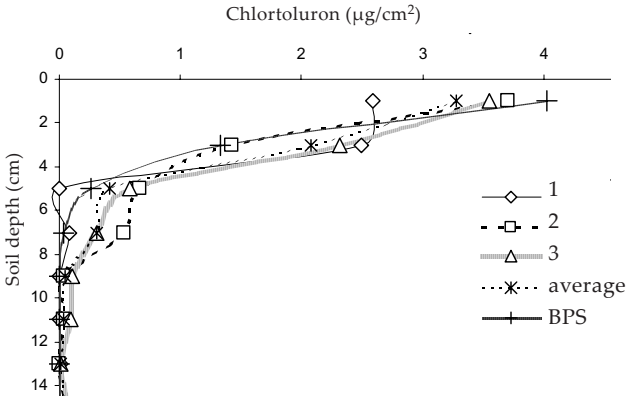

Figure 5. Measured and simulated chlortoluron concentrations (expressed as total amount of solute per mass unit) in the soil profile 35 days after application in Haplic Cambisol: 1, 2 and 3 – measurement at 3 sampled positions, average – averages from this three measurements, BPS – predicted concentrations using the BPS model

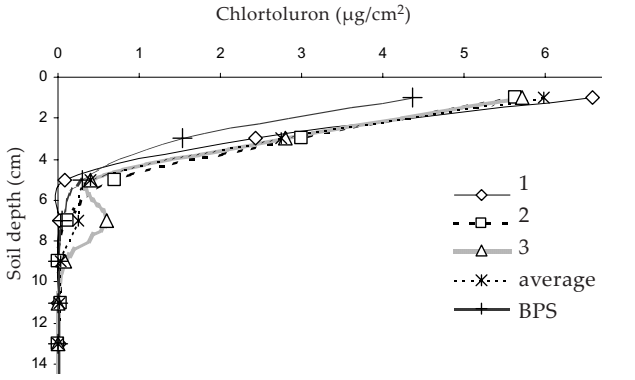

Figure 6. Measured and simulated chlortoluron concentrations (expressed as total amount of solute per mass unit) in the soil profile 35 days after application in Haplic Stagnosol: 1, 2 and 3 – measurement at 3 sampled positions, average – averages from this three measurements, BPS – predicted concentrations using the BPS model

higher than 100%. A similar effect was described by Zander et al. (1999). They observed 101% of remaining chlortoluron in the soil profile 33 days after the application. They explain such an effect by chlortoluron washing down from the plants during the experiment. In our case the main reason is probably the herbicide transport through the preferential paths quickly to the depth, deviation of the solute flow from the vertical axes and low herbicide degradation rates in lower layers. The total amounts of chlortoluron in the soil profiles (0–30 cm) at all 3 positions (Figure 2) show different variability of chlortoluron content in the monitored soil types. The highest variability occurred in Greyic Phaozem, the lowest in Haplic Stagnosol. Figures 3–7 show the chlortoluron concentrations in the soil profiles at 3 sampled positions for each monitored location. The average observed values and chlortoluron concentrations predicted using the BPS model are also presented in those figures. Considerably different herbicide distributions were observed at three positions of the same locations. Such variability is caused by the heterogeneity of the soil profile and by an uneven distribution of chlortoluron on the soil surface. The high variability in Greyic Phaozem is attributed to the preferential flow that differently influenced solute transport at each sampled position. The simulated chlortoluron concentrations approximately follow the measured data except in Greyic Phaozem, where a preferential flow highly influenced solution transport. The BPS model slightly overestimated herbicide mobility in Albic Luvisol. Simulated concentrations in Haplic Stagnosol are underestimated because the solute accumulation in the reduced flow domain was not considered. However, closer correlation was not

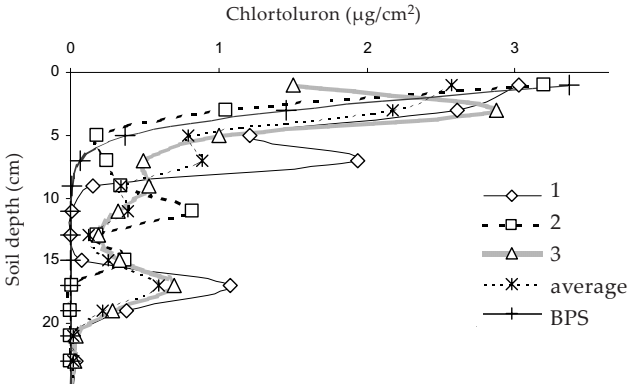

Figure 7. Measured and simulated chlortoluron concentrations (expressed as total amount of solute per mass unit) in the soil profile 35 days after application in Greyic Phaozem: 1, 2 and 3 – measurement at 3 sampled positions, average – averages from this three measurements, BPS – predicted concentrations using the BPS model

expected, since the general inputs of the physical and hydraulic soil properties stored in the soil database were used for simulation. In addition, BPS model cannot describe the preferential flow. Special models have to be used to predict solute transport affected by preferential flow as was shown in Kodešová et al. (2005). The BPS model with the soil database can be used for estimation of the chlortoluron transport. The proper application of the model as well as the improvement of procedures for estimation of the soil hydraulic and solute transport properties should be investigated further.

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ABSTRAKT

Chování chlortoluronu v pěti různých typech půd

Na pěti půdních typech v různých klimatických podmínkách byl sledován transport chlortoluronu. Experimentálně bylo zjištěno, že mobilita chlortoluronu u sledovaných půdních typů stoupá v řadě: Albic Luvisol = Haplic Luvisol < Haplic Cambisol < Haplic Stagnosol < Greyic Phaozem. Na půdním typu Haplic Stagnosol byla zjištěna výrazně vyšší koncentrace chlortoluronu v povrchové vrstvě, což je pravděpodobně způsobeno vysokým podílem skeletu (30–40 %). Celkové množství chlortoluronu v půdním profilu na sledovaných půdních typech (Albic Luvisol 46,06 %, Haplic Luvisol 54,6 %, Haplic Cambisol 65,01 %, Haplic Stagnosol 74,99 % Greyic Phaozem 102,91 %) odpovídá zjištěné mobilitě pesticidu na těchto půdách. Nejvyšší stupeň degradace chlortoluronu byl zjištěn v lokalitách, kde byl herbicid vzhledem ke své nízké mobilitě koncentrován ve svrchní vrstvě půdního profilu. Na půdním typu Greyic Phaozem převyšovala zjištěná koncentrace pesticidu v půdním profilu 100 %, což bylo způsobeno transportem pesticidu preferenčními cestami a nižší degradací ve spodních vrstvách. Rozdíly koncentrací herbicidu ve třech odběrových bodech na každé sledované lokalitě jsou způsobeny heterogenitou půdy a pravděpodobně i nerovnoměrnou aplikací herbicidu. Pro předpověď transportu chlortoluronu v půdě byl použit matematický model BPS (Kozák and Vacek 1996), který je propojen s půdní databází (Kozák et al. 1996). S výjimkou půdního typu Greyic Phaozem, u něhož se výrazně projevilo preferenční proudění, se koncentrace předpověděné modelem BPS přibližně shodují s koncentracemi zjištěnými experimentálně. Matematický model proto může být využit pro přibližný odhad transportu chlortoluronu v půdě.

Klíčová slova: pesticidy; chlortoluron; degradace; transport roztoku; polní a matematické studie

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