Field Study of Chlorotoluron Transport and its Prediction by the BPS Mathematical Model

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Abstract: The chlorotoluron transport in the soil profiles was studied under field conditions on three different soil types of the Czech Republic. The herbicide was applied on 21. 4. 2005 on a four-square meter plot using an application rate of 2 kg/ha. Soil samples were taken on days 35 and 150 from the herbicide application to study the remaining chlorotoluron distributions in the soil profiles. The chlorotoluron distributions in the monitored soils were very similar 35 days after the herbicide application. The major part of chlorotoluron was detected in the top layer of the soil profile (0–8 cm). The highest concentration was obtained in the top 2 cm layer and it decreased gradually with the depth. The percentages of the remaining chlorotoluron 35 days after the herbicide application were similar in Haplic Luvisol (29.97%) and Greyic Phaeozem (30.78%), and slightly higher in Haplic Cambisol (38.58%). The chlorotoluron distributions in the monitored soils differed considerably 150 days after the herbicide application. Chlorotoluron was detected in the entire monitored soils profiles (0–50 cm). The highest concentration was found in all cases in the top 2 cm layer and it decreased gradually with the depth to the depth of approximately 10 cm. Below this level, the herbicide contents were low and the values oscillated randomly. The percentages of the remaining chlorotoluron 150 days after the herbicide application were in the increasing order: Greyic Phaeozem < (5.45%) < Haplic Luvisol (11.7%) < Haplic Cambisol (17.48%). The BPS mathematical model connected with the soil database was used to simulate the chlorotoluron distribution 35 and 150 days after the herbicide application. The comparison of the measured and simulated data indicated probably varying chlorotoluron half-life during the experiment. The results showed that, if the chlorotoluron half-life is estimated based on the remaining chlorotoluron content in the soil profile on the 150th day after the herbicide application, the simulated herbicide content on the 35th day is twice as high as the measured one. On the other hand, if the half-life degradation of chlorotoluron is estimated based on the remaining chlorotoluron content in the soil profile on the 35th day, the herbicide is almost totally degraded on the 150th day of the model simulation.

Keywords: chlorotoluron; contaminant transport; field study; half-life degradation; herbicides; mathematical model BPS

Soil and groundwater contamination with pesticides used in agriculture is an environmental problem worldwide. In this study, the herbicide chlorotoluron was tested. Total chlorotoluron consumption in the Czech Republic in 2005 was 111 069.6 kg according to the State Phytosanitary Administration (2005). Chlorotoluron is the fourth most frequently used herbicide in the Czech Republic used to control cereals weeds (Glyphosate-IPA, 149 852.4 kg; Isoproturon, 137 614.3 kg; MCPA, 94 301.7 kg and Chlorotoluron, 94 286.3 kg). The degree of pesticides losses varies from soil to soil, depending on the structure quality and organic carbon content. Many authors reported that the amount of rainfall immediately after the pesticide application is the most important for pesticide leaching. As presented by Renaud *et al.* (2004), the pesticide movement is affected by the soil

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hydraulic properties (the soil texture, structure, and occurrence of preferential flow), the interaction between the sorption capacity of the solute and soil properties, degree of degradation of bulk residues in soil, and chemical specific process reducing the relative availability of chlorotoluron for leaching over time.

The research into pesticides behaviour under field conditions, which is in progress now with some results presented here, started as early as in 1994. In that year, the residual concentrations of herbicide Atrazin 135 days after the application in Greyic Phaeozen in Kutná Hora were studied experimentally and simulated by BPS mathematical model (Kozák & Vacek 1996). The measured values agreed well with the values estimated by the model for the warm climatic period of the area. The experiments then continued in 1997, 2004 and 2005. In those years, chlorotuloron was used. This herbicide was applied in Haplic Chernozem in Tišice in 1997 and the residual concentrations of chlorotoluron were determined on 119th day after the herbicide application. The chlorotoluron distribution measured in the soil profile was compared with the data simulated using HYDRUS-1D (Šimůnek & van Genuchten 2008; Šimůnek *et al.* 2008) as referred to in Kodešová *et al.* (2004). The applied model could not approximate the observed values more closely since the preferential flow affected the actual herbicide transport in the soil. Therefore, the dual-permeability model in HYDRUS-1D was used for the simulation (Šimůnek & van Genuchten 2008). This model that had been designed to simulate the preferential flow and solution transport was used for a better prediction of the herbicide behaviour in this soil (Kodešová *et al.* 2005). The results of the field experiments carried out on five different soil types in 2004 were published by Kočárek *et al.* (2005). Chlorotoluron distribution in the soil profile 35 days after the herbicide application was studied. It was observed that the mobility of chlorotoluron increased in the following order: Haplic Luvisol 1 in Hněvčeves = Haplic Luvisol 2 in Kostelec nad Orlicí < Haplic Cambisol in Humpolec < Dystric Cambisol in Vysoké nad Jizerou < Greyic Phaeozem in Čáslav. The highest level of the herbicide degradation was observed in those areas where the herbicide was concentrated in the upper layer of the soil profile. The concentrations of the herbicide in the soil profiles in 2004 were simulated by the BPS model. The predicted values agreed approximately with the measured values with the exception of Greyic Phaeozem where the preferential flow highly affected the herbicide transport. The entire set of the experimentally determined residual concentrations on days 5, 13, 21, and 35 after the herbicide application as obtained in 2004 were evaluated in Kočárek *et al.* (2006). The data obtained with Haplic Luvisol, Greyic Phaeozem, and Haplic Cambisol were compared with the simulated results of single-porosity, dual-porosity and dual-permeability models in HYDRUS-1D (Kodešová *et al.* 2008). The concentrations simulated by the dual-permeability model were the closest to the measured values for Greyic Phaeozem and Haplic Cambisol. In addition, the transport of chlorotoluron was experimentally studied in undisturbed soil columns (from each diagnostic horizon of all 3 soil types) by Kodešová *et al.* (2009). In this case, the preferential water flow affected the herbicide distribution within the columns and herbicide leaching from the soil samples. The dual-permeability model in HYDRUS -1D and two site sorption model (van Genuchten & Wagenet 1989) were applied to obtain a better correlation between the measured and simulated data. The impact of varying soil micromorphology on the soil hydraulic properties and, consequently, on the water flow and herbicide transport observed in the field and laboratory was summarised by Kodešová (2009).

The experimental data obtained in the field in 2005 are presented in this study. The experiments were performed similarly as in the previous years on the three soil types that had been studied also in 2004. They were chosen for examples where different chlorotoluron behaviour was observed. The aim of this study was: (1) determination of the chlorotoluron distribution 35 and 150 days after the herbicide application in three different soil units under varying climatic conditions, (2) comparison of the experimental data obtained in 2004 and 2005, (3) validation of the BPS mathematical model (Kozák & Vacek 1996) for the prediction of the chlorotoluron distribution in these soils for short (35 days) and extended (150 days) time periods.

MATERIAL AND METHODS

The experiments were carried out on the tillage field on the soil types Haplic Luvisol in Hněvčeves,

Haplic Cambisol in Humpolec, and Greyic Phaeozem in Čáslav. The elevations above the see level were: Haplic Luvisol 300 m a.s.l., Haplic Cambisol 270 m a.s.l. and Haplic Cambisol 500 m a.s.l. Chlorotoluron was applied on 21st April in 2005 and the soil samples were taken on the 35th and 150th days after the application. Two litter of water with 1 g of chlorotoluron was applied on experimental plots sized 2 × 2 m. This dose corresponds to the usually applied Syncuran amount of 2.5 kg/ha. One litter of fresh water was used to wash down the herbicide from the plants and ensure the solution inflow into the soil. Soil samples from layers 2 cm thick (to the depth of 20 cm) and 5 cm thick (from 20 cm to the total depth 50 cm) were taken at five positions from each experimental plot.

The soil samples were analysed in the laboratory to determine chlorotoluron distributions in the soil profiles using the method described in Kočárek *et al.* (2005). The soil samples were dried, ground and sieved through 1-mm sieve. The total amount of chlorotoluron in each soil sample was determined as follows. 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 h into a shaking apparatus. After that, the analysed soil sample was centrifuged 30 min at 13 800 rotations per min using centrifuge Sigma 3-18K (Sigma-Aldrich, Osterode am Harz, Germany). The chlorotoluron concentration in the methanol extract was determined by the High Performance Liquid Chromatography (HPLC). The total amount of chlorotoluron present in the soil sample was expressed as the total amount of solute per mass unit (μg/g). The average values of 5 sample points in each layer were calculated.

The HPLC instrument from Dionex (Sunnyvale, USA) was used for the chlorotoluron determination. The instrument was assembled using P680 HPLC Pump. The mobile phase was prepared by mixing together 600 ml of methanol, 400 ml of redistilled water, and 6 ml of NH_4OH. The flow rate of this mobile phase was maintained at the level of 1 ml/min. The samples were injected via the automatic sampler ASI-100 Automated Sample Injector. The separation took place in the C18 Varian (Lake Forest, USA) HPLC ChromSpher Pesticide Columns (250 × 4.6 mm) placed in the Thermostatted Column Compartment TCC-100 temperated to 20°C. To prolong the lifetime of this column, the ChromSep Guard Column SS 10 × 3MM (Varian, Lake Forest, USA) was used. The detection of chlorotoluron was performed on line in UV region (310 nm) by means of PDA-100 Photodiode Array Detector. The signal from the detector was processed and stored by chromatographic software Chromeleon, version 6.70 (Dionex).

The BPS mathematical model (Kozák & Vacek 1996) was used to simulate the herbicide transport in the soil types studied. This model simulates the water flow and transport of the dissolved substances in water, mainly pesticides, in one-dimensional soil

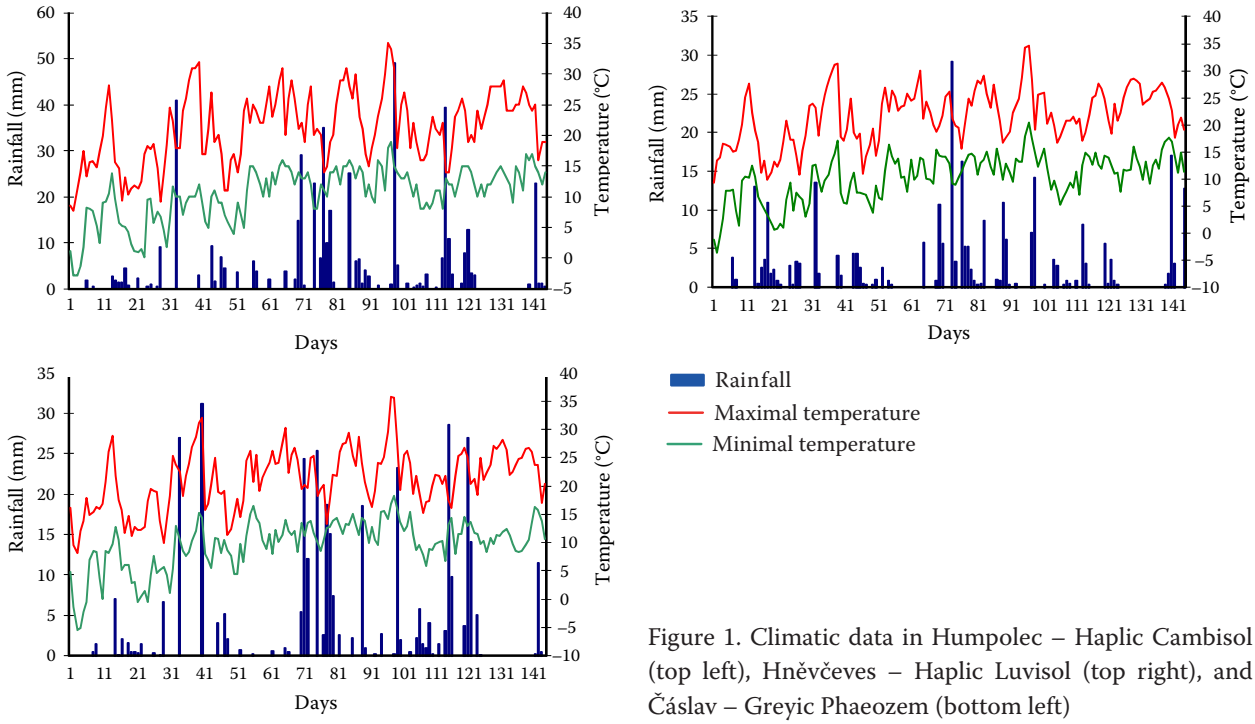

Figure 1. Climatic data in Humpolec – Haplic Cambisol (top left), Hněvčeves – Haplic Luvisol (top right), and Čáslav – Greyic Phaeozem (bottom left)

Table 1. Measured values used for BPS model application

	pH_{KCl}	CEC (meq/100 g)	C_{OX} (%)
Haplic Cambisol	4.4	26.0	1.63
Haplic Luvisol	5.6	24.0	1.03
Greyic Phaeozem	6.5	29.7	1.35

profile divided into layers 2 cm thick. The principle of the soil water balance is a cascade of overflowing buckets. The mathematical modelling with BPS is based on the assumption of leakage from the separated layers if the field capacity is exceeded. The solution transport is controlled only by convection. No solute dispersion is assumed. The daily precipitations and maximal and minimal temperatures were measured at each location (Figure 1). Evapotranspiration was estimated by the BPS model assuming minimum and maximum daily temperatures. The soil hydrophysical and chemical properties were determined for each location. However, the mean values of hydrophysical properties for each soil type stored in the soil database PUGIS (Kozák *et al.* 1996), which is connected with BPS model, were used to study the potential of such inputs for the general characterisation of the herbicide transport in specific soil types. The adsorption coefficients in the surface horizons were predicted using the pedotransfer rules (Kozák & Vacek 2000) from the measured values of CEC (cation exchange capacity), pH_{KCL} (exchangeable acidity), C_{ox} (oxidizable carbon) (Table 1), and clay content from the PUGIS database. The adsorption coefficients in the subsurface horizons were predicted using the pedotransfer rules from the CEC, pH_{KCL}, C_{ox} and clay content values stored in the PUGIS database. The chlorotoluron half-lives were estimated assuming either 150th day or 35th day chlorotoluron contents in the soil profile.

RESULTS AND DISCUSSION

The resulting average chlorotoluron concentrations are presented in Figure. 4. While the experimental data obtained on the 35th day after the herbicide application (Figure 2 right) for different soil types were similar, the data obtained on the 150th day (Figure 2 left) were significantly different. The major mass of chlorotoluron in each monitored soil type on the 35th day was detected in the upper 8 cm of the soil profile. These results correspond with the results presented by Kočárek *et al.* (2005, 2006) for Haplic Luvisol (classified as Albic Luvisol in these studies – **soil was reclassified after the new sample analysis**) and Haplic Cambisol. On the other hand, the chlorotoluron behaviour in Greyic Phaeozem was different in 2004, when the herbicide moved to the depth of 20 cm.

Considerable differences between the chlorotoluron distribution in the soil profiles of the monitored soils were found on the 150th day. Chlorotoluron was detected in the entire soil profiles (0–50 cm). Chlorotoluron was not gradually distributed in the soil profile as would be expected assuming a uniform water flow and solute transport in a rigid porous medium. The highest chlorotoluron concentrations were found in all cases in the top 2 cm layer and they decreased gradually with the depth to the depth of approximately 10 cm. Below this level, the herbicide contents oscillated randomly with gaining depth especially in Greyic Phaeozem and Haplic Luvisol. The herbicide trans-

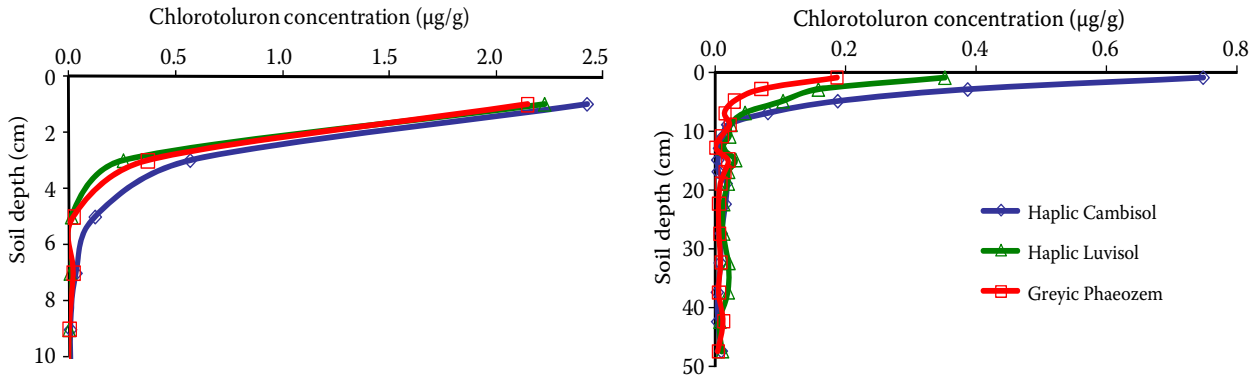

Figure 2. Chlorotoluron distributions in the soil profile on 35th (left) and 150th (right) days after the herbicide application on monitored soil types

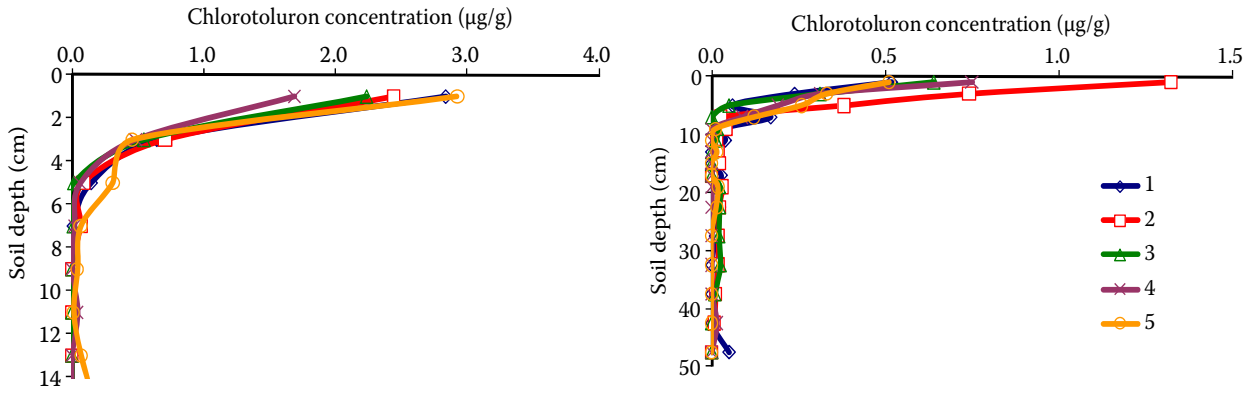

Figure 3. Chlorotoluron distributions in the soil profile on 35th (left) and 150th (right) days after the herbicide application on Haplic Cambisol in five sampling positions

port in those soil profiles was probably influenced by the preferential flow. A more regular decrease of the chlorotoluron concentration with the gaining of soil depth was found in Haplic Cambisol.

Considerably different herbicide distributions were observed at the five positions of the same locations (Figures 3–5). The variability in Haplic Luvisol and Greyic Phaeozem was higher than that in Haplic Cambisol. Such a variability is caused by the heterogeneity of the soil surface and soil profile, uneven distribution of chlorotoluron on the soil surface during the application, and varying occurrence of the preferential flow. Similar differences at three sampling points of five different experimental plots were described by Kočárek *et al.* (2005), where the highest variability of chlorotoluron distributions on the 35th day after the herbicide application was observed in Greyic Phaeozem. The chlorotoluron distribution variability was not so evident in other two soil profiles.

The total amount of chlorotoluron in the soil profiles (0–50 cm) and the percentages of the chlorotoluron remaining from the theoretically applied dose were calculated using the bulk density of soil (Figure 6). Total amounts of the remaining chlorotoluron in five sampling points of each experimental plot on the 35th day after chlorotoluron application were very different (Figure 6 left). The average values of the remaining chlorotoluron in the soil profile were 7.492 µg/cm^2 for Haplic Luvisol, 7.696 µg/cm^2 for Greyic Phaeozem, and 9.644 µg/cm^2 for Haplic Cambisol. The percentages of the chlorotoluron remaining in the soil profile from the theoretically applied dose were 29.97% in Haplic Luvisol, 30.78% in Greyic Phaeozem and 38.58% in Haplic Cambisol. These results are considerably low in comparison with the results observed in 2004 by Kočárek *et al.* (2005). In this study, the percentage of the remaining chlorotoluron 35 days after the application were higher because of the postemergent herbicide application and consequent retardation of the degradation of chlorotoluron sticking in the plant leaves. The percentages of the remaining chlorotoluron 35 days after the herbicide

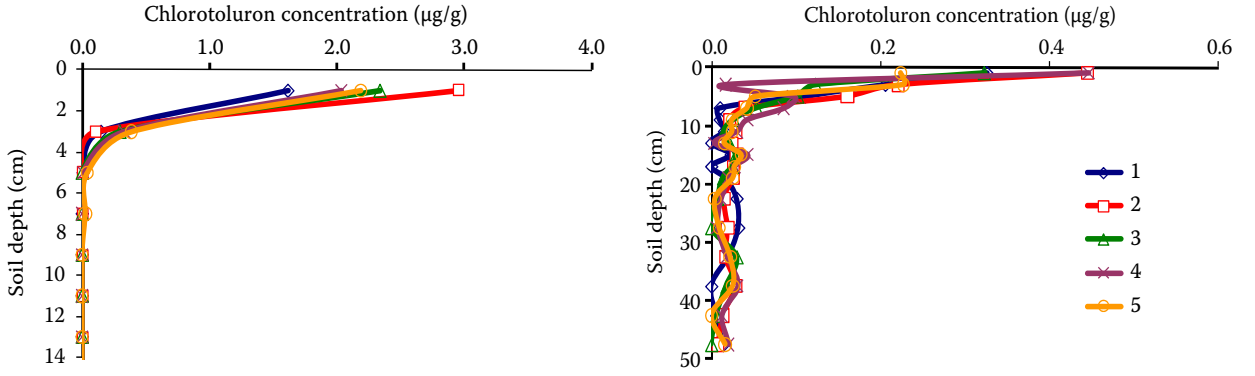

Figure 4. Chlorotoluron distribution in the soil profile on 35th (left) and 150th (right) days after the herbicide application on Haplic Luvisol in five sampling positions

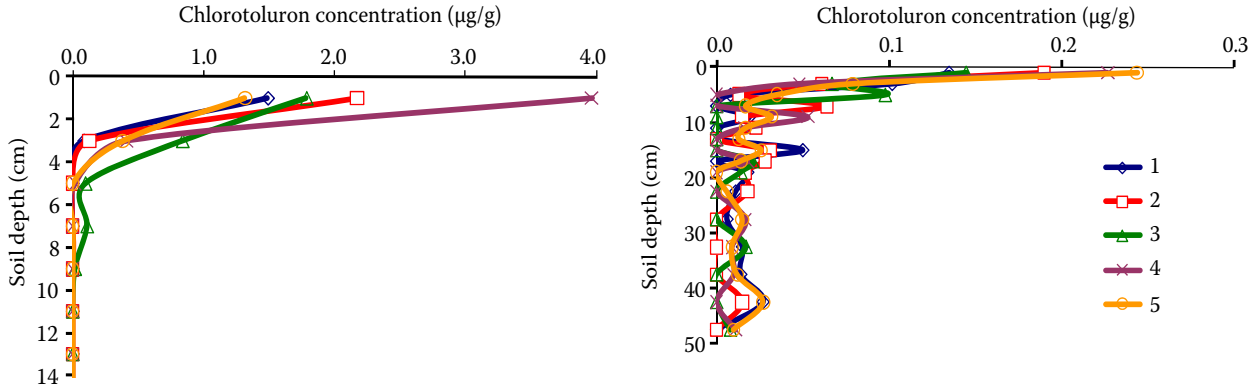

Figure 5. Chlorotoluron distribution in the soil profile on 35th (left) and 150th (right) days after the herbicide application on Greyic Phaeozem in five sampling positions

application were: 46.1% in Haplic Luvisol, 65.0% in Haplic Cambisol, and 102.9% in Greyic Phaeozem. As reported by Kočárek *et al.* (2005), the very high value obtained for Greyic Phaeozem was probably caused by the preferential flow, deviation of the solute flow from the vertical axis, and low herbicide degradation rates in lower layers.

The values of total amounts of the remaining chlorotoluron in the soil profiles at all five sampling positions on the 150th day after the application in 2005 are shown in Figure 6 (right). The total chlorotoluron contents at five sampling positions of each monitored soil type were similar except for one sampling position in Haplic Cambisol. The highest degradation was observed in Greyic Phaeozem and the lowest one in Haplic Cambisol. The amounts of the remaining chlorotoluron were 1.362 µg/cm^2 in Greyic Phaeozem, 2.926 µg/cm^2 in Haplic Luvisol, and 4.374 µg/cm^2 in Haplic Cambisol. The percentages of the chlorotoluron remaining in the soil profile from the theoretically applied dose were 5.45% in Greyic Phaeozem, 11.7% in Haplic Luvisol, and 17.48% in Haplic Cambisol.

The BPS mathematical model (Kozák & Vacek 1996) connected with the soil database (Kozák *et al.* 1996) was used to simulate chlorotoluron distribution on the 35th and 150th days after the herbicide application. To obtain the best agreement between the measured and simulated chlorotoluron distributions in the soil profile 150 days after the herbicide application, the half-life of chlorotoluron degradation was set equal to 40 days in Haplic Luvisol and 35 days in Haplic Cambisol and Greyic Phaeozem. Figure 7 shows the experimental data and the simulated data using BPS. The predicted values approximately correspond with the data measured on the 150th day after the herbicide application in Greyic Phaeozem and Haplic Luvisol. The predicted chlorotoluron concentration 150 days after the herbicide application in Haplic Cambisol was moderately over estimated. However, the predicted chlorotoluron distribution 35 days

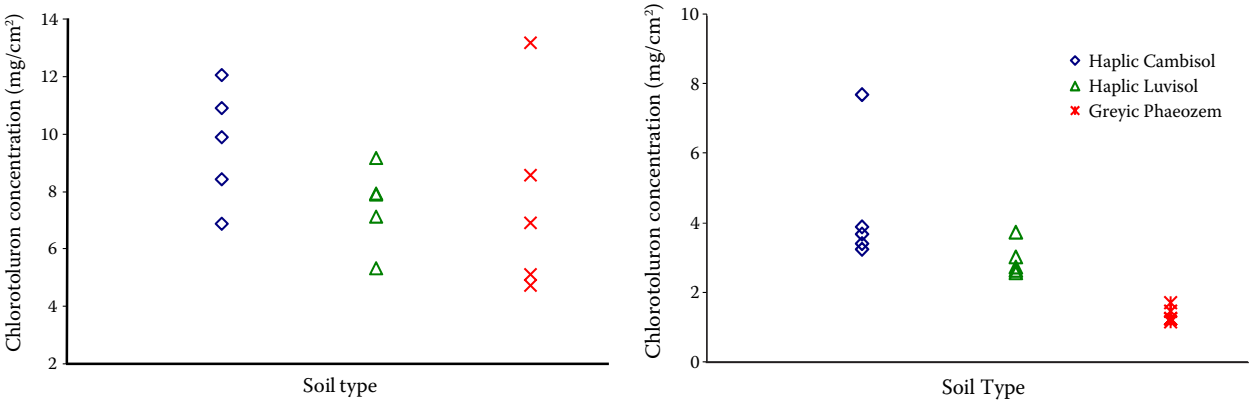

Figure 6. Total amount of the remaining chlorotoluron in the soil profile on 35th (left) and 150th (right) days after the herbicide application

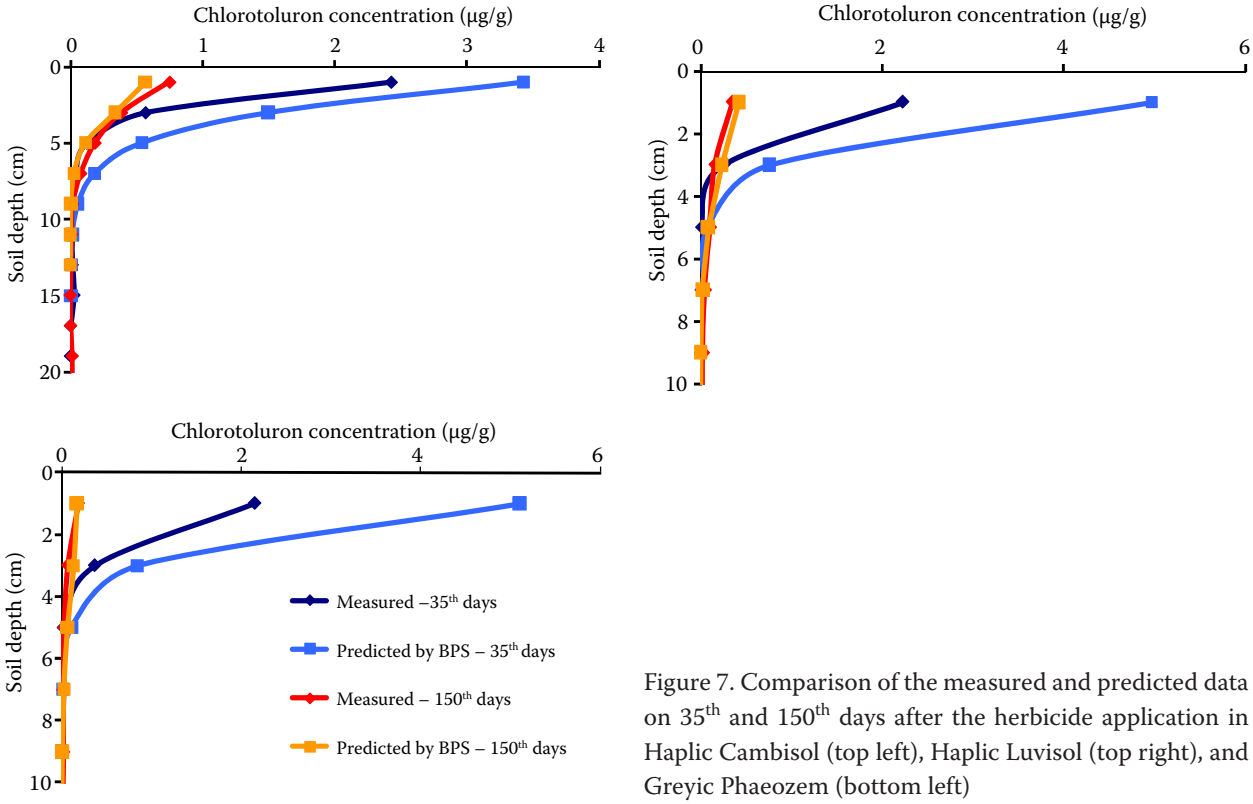

Figure 7. Comparison of the measured and predicted data on 35th and 150th days after the herbicide application in Haplic Cambisol (top left), Haplic Luvisol (top right), and Greyic Phaeozem (bottom left)

after the herbicide application was in all cases approximately twice as high as measured values. To obtain the best agreement between the measured and simulated chlorotoluron distribution in the soil profile 35 days after the herbicide application, the half-life of chlorotoluron degradation was set equal to 20 days in Haplic Cambisol, 14 days in Haplic Luvisol, and 12 days in Greyic Phaeozem. Due to such high degradation rates, the herbicide during the simulation period almost totally degraded and chlorotoluron concentrations on the 150th day in the model simulation (not shown here) were lower then 0.016 µg/g in Haplic Cambisol and 0.002 µg/g in Haplic Luvisol, while no chlorotoluron in the soil profile was obtained in Greyic Phaeozem. The measured and simulated data presented in this study indicate varying values of chlorotoluron half-life degradation during the experiment. The chlorotoluron half-life degradation was influenced by many factors, including varying soil-water contents and temperatures during the experiment, varying bacteria species and their contents in the course of time, different degradation rates within the soil profile, impact of crop canopy, and a lower availability of chlorotoluron absorbed on soil particles for the degradation processes during the second part of experiment. On the other hand, the chlorotoluron half-life estimated from the chlorotoluron content in the soil profile observed on the 35th day was very low. More realistic estimates (38 days in Haplic Cambisol and 34 days in Haplic Luvisol) were obtained assuming the data observed on the 35th day in 2004. These chlorotoluron half-lives are similar to the values estimated from the data observed on the 150th day in 2005 and they also correspond to the usually presented values of 34–45 days (Footprint 2009) and 30–40 days (Tomlin 2007). Since the soil and solute properties, which are variable in time, cannot be applied in the BPS model, the higher values of chlorotoluron half-life are more suitable for the simulation of herbicide behaviour in the soil types studied.

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