

Impact of pre-emergent and post-emergent herbicide application on the rate of chlorotoluron degradation in soil

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Abstract The rates of chlorotoluron degradation in different soil units under different climatic conditions were studied during two years. The experiments were carried out in the soil units Haplic Cambisol (Humpolec), Haplic Phaeozem (Čáslav), Haplic Luvisol (Hněvčeves) and Dystric Cambisol (Vysoké nad Jizerou). Two liters of water containing 1 g of chlorotoluron was applied on experimental plots 2 × 2 m. The herbicide was applied post-emergently on May 5th 2004 to the winter wheat grow and soil samples were taken on the day of application and 5, 13, 21 and 35 days after the herbicide application. The herbicide was applied pre-emergently on April 21st 2005 to the barley grow and soil samples were taken on the day of application and 7, 35, 63 and 148 days after the herbicide application.

The total chlorotoluron amount determined 35 days after the herbicide application in individual soil units implies that the rates of chlorotoluron degradation were higher in 2005 than degradation rates in 2004. It could be suggested on the basis of the climatic data, that the chlorotoluron degradation rates would be similar in both years (with the exception of Haplic Phaeozem). The low chlorotoluron degradation rates in 2004 were probably caused by the fact that the chlorotoluron applied on the plant surface in 2004 didn't degrade as quickly as the chlorotoluron applied in the soil surface in 2005. The other possible explanation could be that the mature growth, in which the chlorotoluron was applied in 2004, shaded the soil surface and thus decreased its temperature. The barley transpiration also caused soil moisture decrease. These two factors reduced the microbial degradation rates of chlorotoluron. Furthermore, the shaded soil surface also decreased the possibility of chlorotoluron photodegradation. And finally, the preferential flow could also lower the rate of degradation because of decreased microbial activity in subsurface horizon in Haplic Phaeozem.

Introduction

The degradation rate of pesticide in soil is affected by many factors. The importance of organic matter content, porosity, soil structure, hydraulic conductivity and growth of species where the herbicide was applied was reported by several authors (Kördel et al., 1995; Kozák, 1996; Groen, 1997; Lluch et al., 1997; Beulke et al., 2004; Kodešová et al., 2005). However, the existing literature provides only little information about the impact of the species and growth development in the time of herbicide application.

Pesticides degrade in soil mainly due to the presence of microorganisms. The half life of pesticide is affected by consumption and activity of these microorganisms (Kunc, 1987; Khadrani, 1999; Rouchaud, 2000). However, the availability of the substrate for microbial degradation influences the degradation too (Kunc, 1992). That is why it might be possible that the persistence of pesticides, which do not undergo photodecomposition and volatilization much, can be higher in the case of post-emergent application, mainly because of the availability for microorganisms at that time. The impact of chlorotoluron pre-emergent and post-emergent application is discussed in this study.

Material and methods

The experiments were carried out in the soil units Haplic Cambisol (Humpolec), Haplic Phaeozem (Čáslav), Haplic Luvisol (Hněvčeves) and Dystric Cambisol (Vysoké nad Jizerou). Two liters of water containing 1 g of chlorotoluron were applied on experimental plots 2 × 2 m. The herbicide was applied post-emergently on May 5th 2004 to the winter wheat grow and soil samples were taken on the day of application and 5, 13, 21 and 35 days after the herbicide application. The herbicide was applied pre-emergently on April 21st 2005 to the barley grow and soil samples were taken on the day of application and 7, 35, 63 and 148 days after the herbicide application. Soil samples from layers 2 cm thick (to the depth of 30 cm in 2004 and to the depth of 20 cm in 2005) and from layers 5 cm thick (from the depth of 30-50 cm in 2004 and from the depth of 20-50 cm in 2005) were taken using a sampling probe (at three sampling positions in 2004 and at five sampling position in 2005) of each experimental plot. Cooling box was used to prevent the chlorotoluron degradation during transportation to the laboratory.

The soil samples were analyzed in the laboratory to determine chlorotoluron distributions in the soil profiles as well as the gravimetric soil moisture content.

The soil samples were dried, grinded and sieved through 1-mm sieve. The chlorotoluron concentration in each soil sample was determined as follows. 5g of dry soil were placed into the 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 samples were centrifuged at 13 800 rpm for 30 minutes. The chlorotoluron concentration in the methanol extract was determined utilizing the HPLC technology. The total amount of chlorotoluron presented in the soil sample was expressed as the total amount of solute per mass unit ($\mu\text{g/g}$).

The average values from 3, respectively 5 samples for each layer were calculated.

Climatic data from each experimental location were recorded during the experiment. The daily rainfalls, maximal and minimal temperatures during the first 35 days of the experiments are shown in Figs. 1-4. Sums of the daily rainfalls, averages of the minimal and maximal temperature are presented in Tab. 1. Soil moisture content observed 35 days after the herbicide application in each sampling position of monitored soil units in 2004 and 2005 is presented in Figs. 5-8.

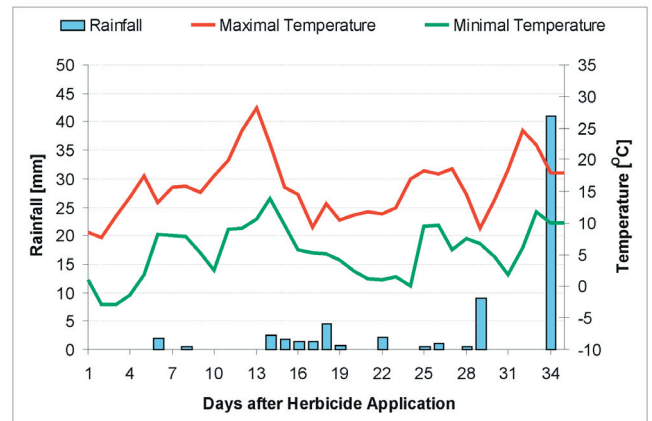
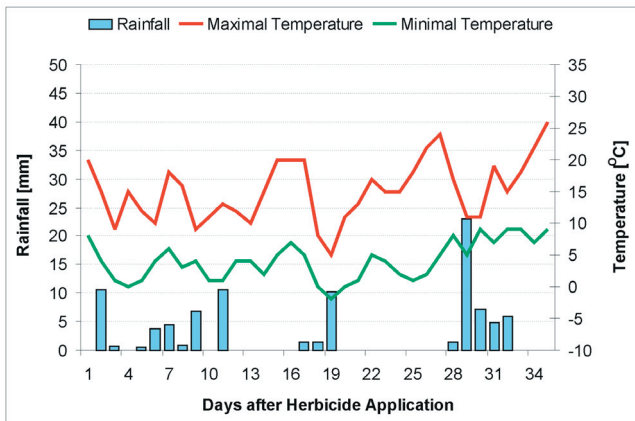


Fig. 1 Climatic data recorded during the first 35 days of the experiments on Haplic Cambisol in 2004 (A) and 2005 (B)

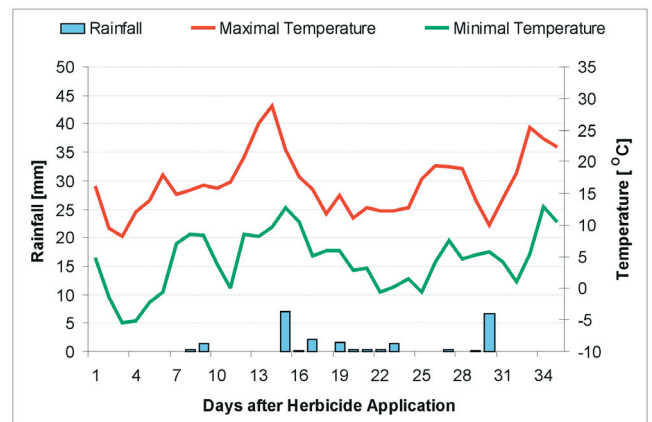
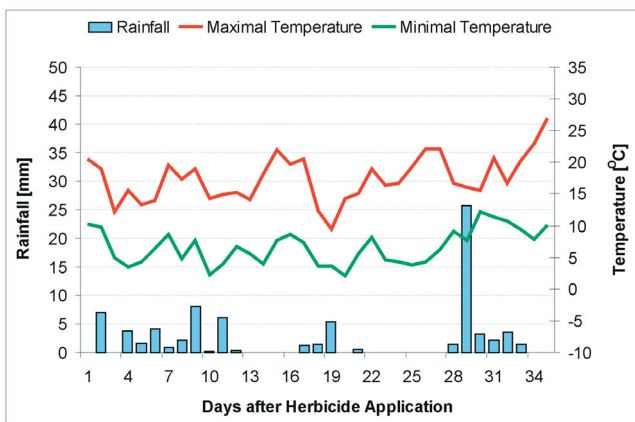


Fig. 2 Climatic data recorded during the first 35 days of the experiments on Haplic Phaeozem in 2004 (A) and 2005 (B)

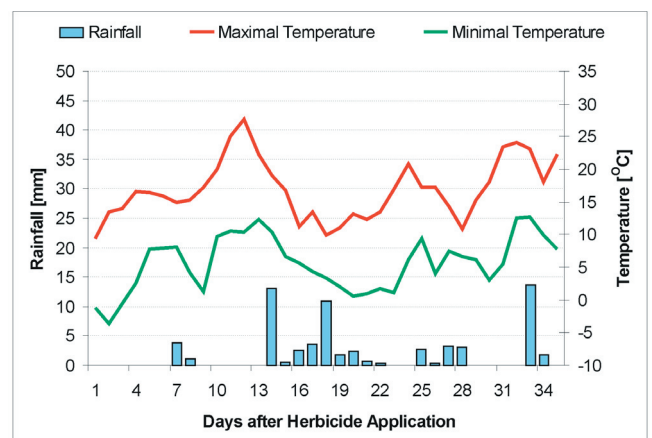
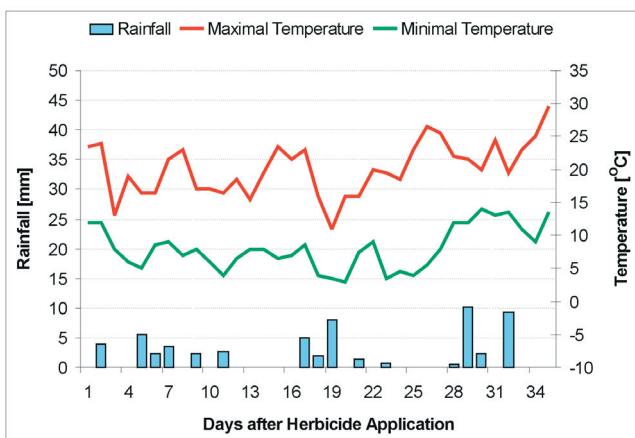


Fig. 3 Climatic data recorded during the first 35 days of the experiments on Haplic Luvisol in 2004 (A) and 2005 (B)

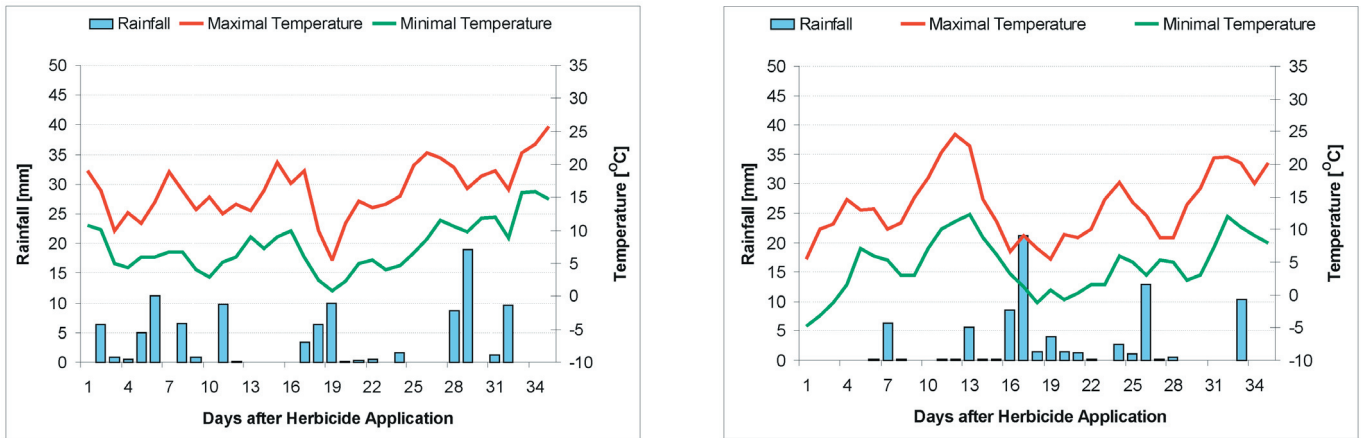


Fig. 4 Climatic data recorded during the first 35 days of the experiments on Dystric Cambisol in 2004 (A) and 2005 (B)

Tab. 1 Sum of rainfall, minimal and maximal temperature observed during the experiments in each soil unit

	Rainfall ? [mm]	Average Minimal Temperature [°C]	Average Maximal Temperature [°C]
Haplic Cambisol 2004	64.9	3.9	14.9
Haplic Cambisol 2005	69.3	5.4	15.8
Haplic Phaeozem 2004	80.3	6.6	17.3
Haplic Phaeozem 2005	22.3	4.4	16.5
Haplic Luvisol 2004	59.7	8.0	20.0
Haplic Luvisol 2005	65.2	5.6	16.9
Dystric Cambisol 2004	101.6	7.5	15.9
Dystric Cambisol 2005	109.3	6.1	15.1

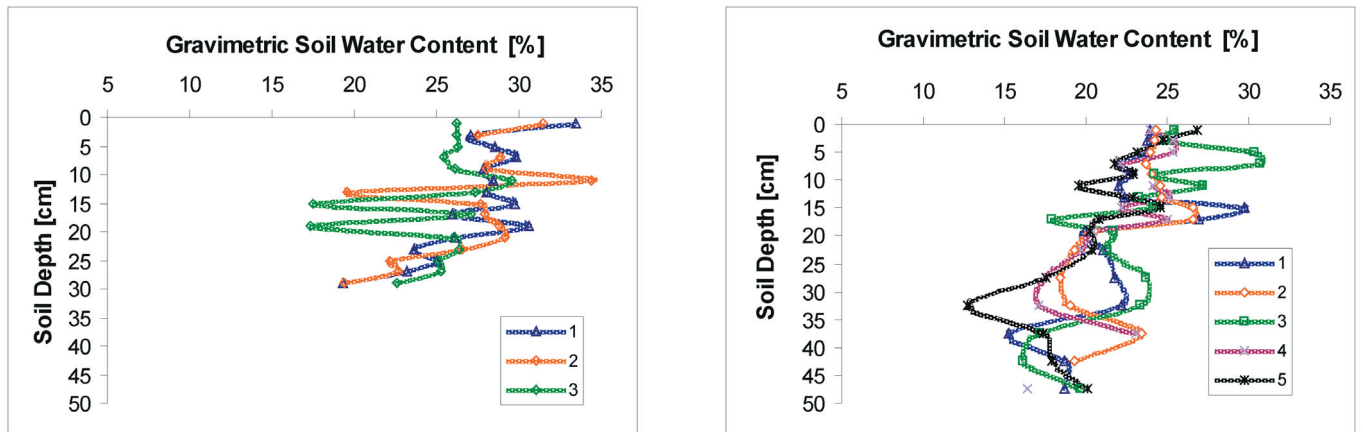


Fig. 5 Soil water contents per mass determined within the soil profile in each sampling position of studied soil 35 days after herbicide application in Haplic Cambisol in 2004(A) and 2005 (B)

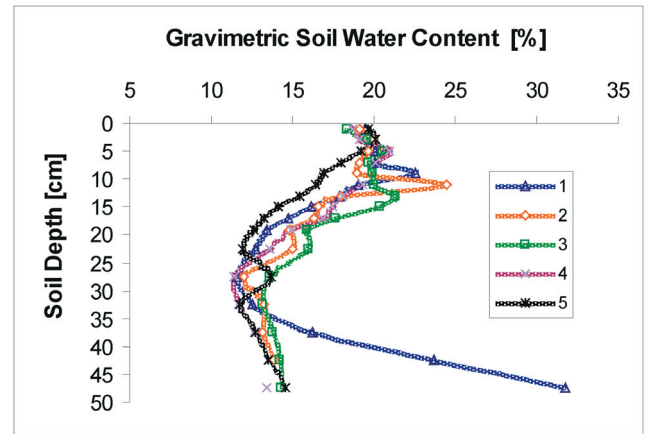
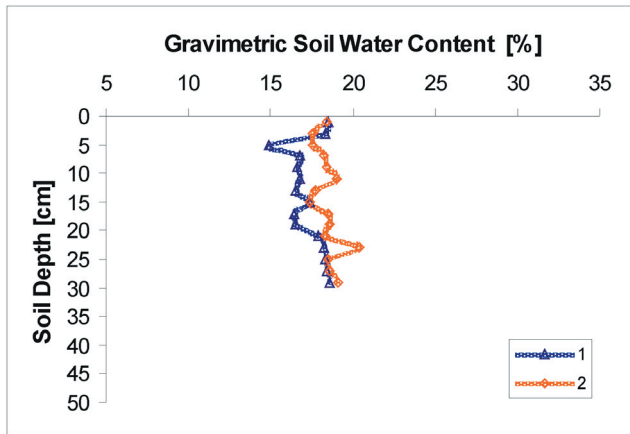


Fig. 6 Soil water contents per mass determined within the soil profile in each sampling position of studied soil 35 days after herbicide application in Haplic Phaeozem in 2004(A) and 2005 (B)

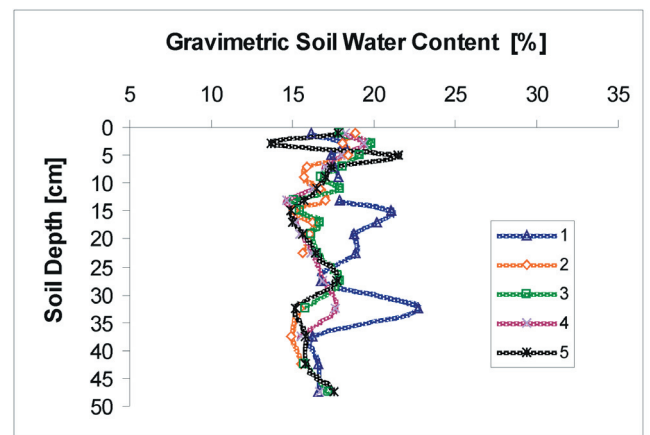
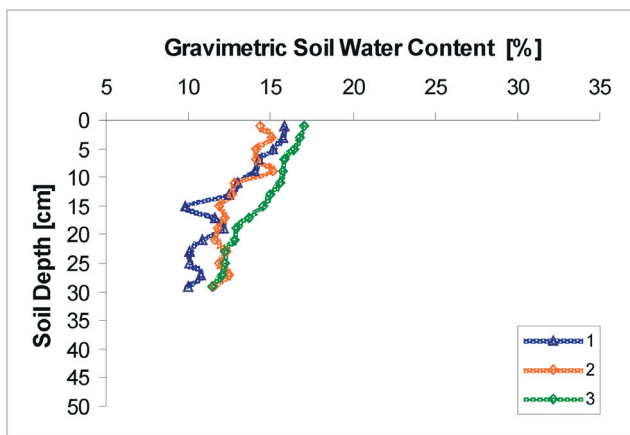


Fig. 7 Soil water content per mass determined within the soil profile in each sampling position of studied soil 35 days after herbicide application in Haplic Luvisol in 2004(A) and 2005 (B)

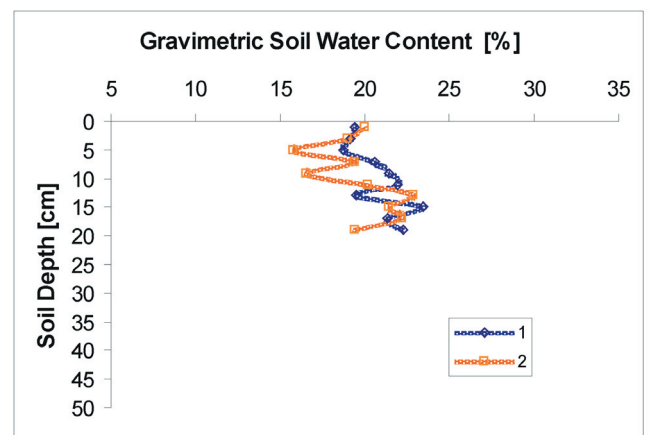
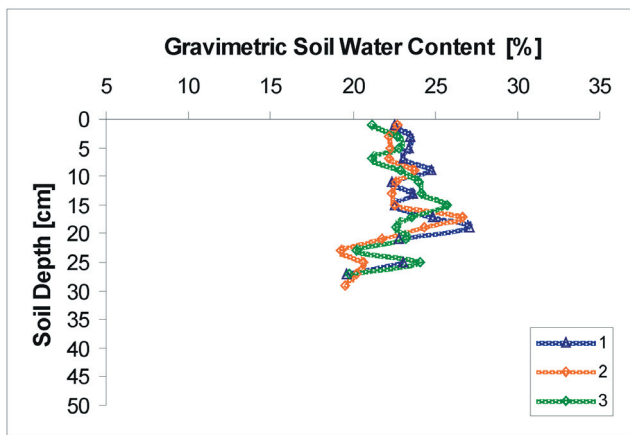


Fig. 8 Soil water contents per mass determined within the soil profile in each sampling position of studied soil 35 days after herbicide application in Dystric Cambisol in 2004(A) and 2005 (B)

Results and discussion

The average chlorotoluron concentrations calculated from the chlorotoluron concentrations detected in all sampling position of monitored soils 35th days after the herbicide application is presented in Fig. 9. Chlorotoluron

distributions in the soil profiles of different monitored soil units were similar in 2005, but there were significant differences between the chlorotoluron distributions in varying soil profiles in 2004.

Chlorotoluron concentrations detected in 2004 were in all soil units higher than chlorotoluron concentrations detected in 2005. The mayor masses of chlorotoluron were detected mainly in the upper 4 cm of the soil profiles in all soil units in 2005. Chlorotoluron distribution in the soil profile of Haplic Luvisol was quite similar in both years. In Haplic Cambisol chlorotoluron was more mobile in 2004 than in 2005 despite the fact that climatic conditions were very similar in both years, due to the lower degradation rate and availability of in water dissolved herbicide for transport. The most significant difference between the chlorotoluron distributions in 2004 and 2005 was determined in Haplic Phaeozem. Chlorotoluron was detected within the whole monitored soil profile (0-50 cm) in 2004. The rapid herbicide transport in the soil profile and uneven distribution of chlorotoluron within the soil profile occurred due to the preferential flow. The difference in the amounts of rainfall (80.3 mm

in 2004 and 22.3 mm in 2005) would also confirm this phenomenon.

Variability of chlorotoluron concentration detected in each sampling position of each soil unite in 2005 was higher than variability of average chlortoluron distribution in different soil types (Figs. 10-13). Such variability is caused by the heterogeneity of the soil profile, by uneven distribution of chlorotoluron on the soil surface during application and varying occurrence of preferential flow. In addition, chlorotoluron can be concentrated in convex places of the experimental plots and can be transported through the soil profile by the path deflected from the vertical axe. The significant differences in soil moisture content observed in each soil layer and sampling position of monitored soils (Figs. 5-8) also indicate the heterogeneity of the soil profiles and different flow of soil solutions through the soil profiles of each monitored soil units.

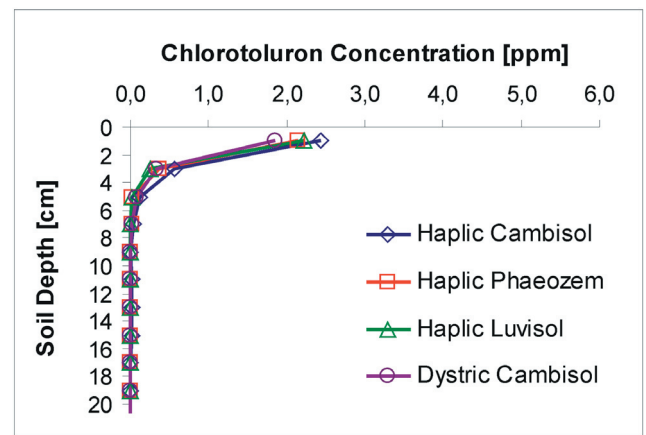
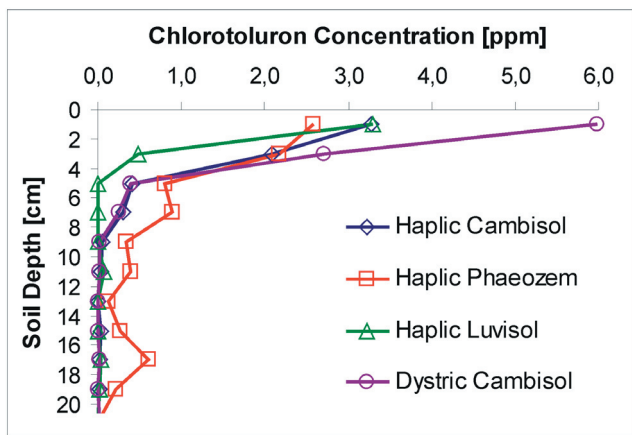


Fig. 9 Chlorotoluron distributions in soil profiles in 2004 (A) and 2005 (B)

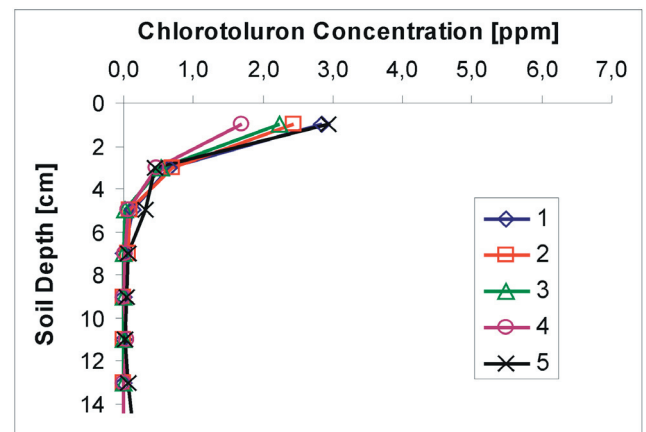
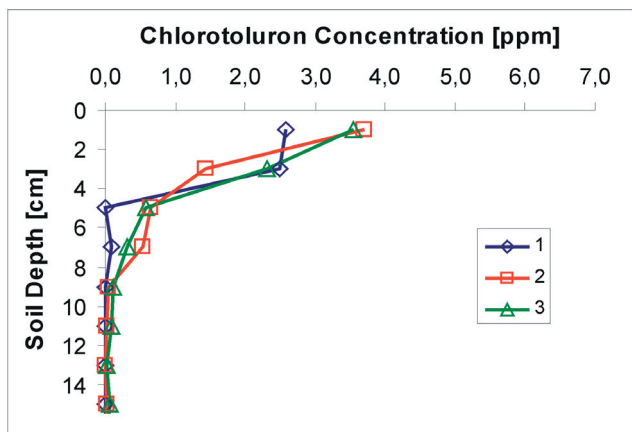


Fig. 10 Chlorotoluron concentrations detected in each sampling position in Haplic Cambisol in 2004 (A) and 2005 (B)

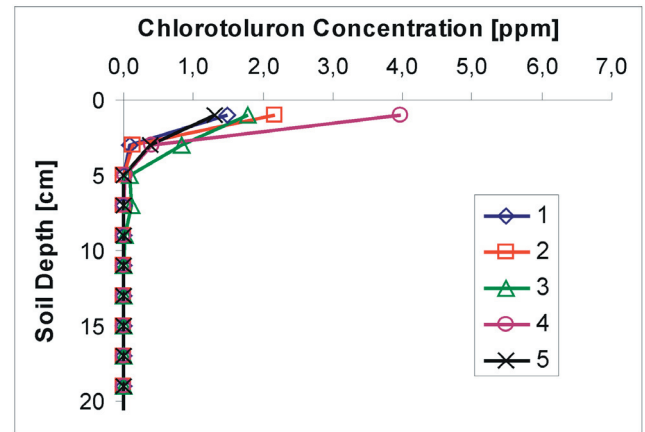
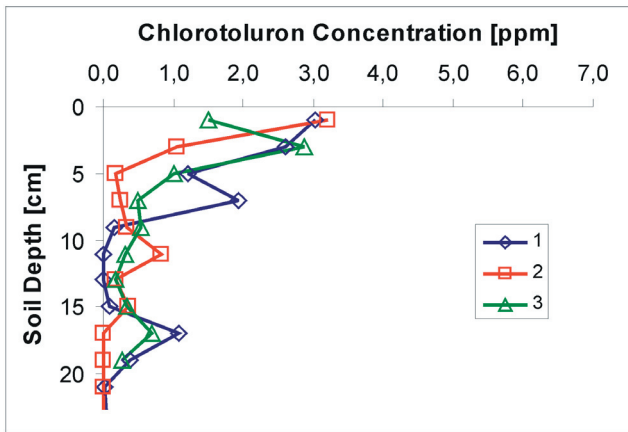


Fig. 11 Chlorotoluron concentrations detected in each sampling position in Haplic Phaeozem in 2004 (A) and 2005 (B)

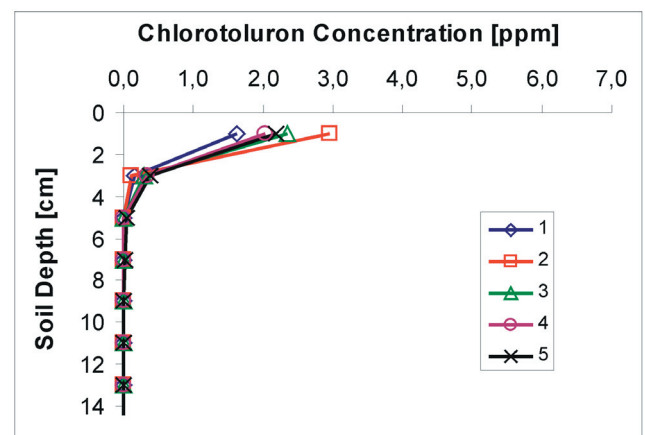
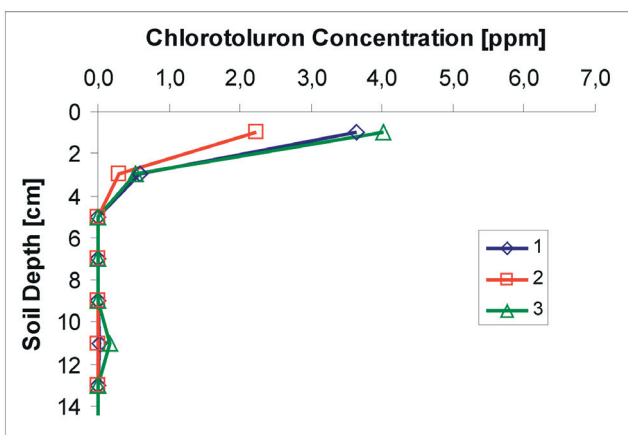


Fig. 12 Chlorotoluron concentrations detected in each sampling position in Haplic Luvisol in 2004 (A) and 2005 (B)

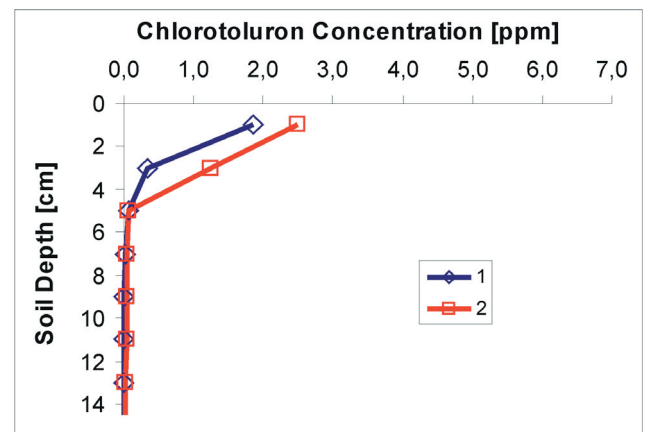
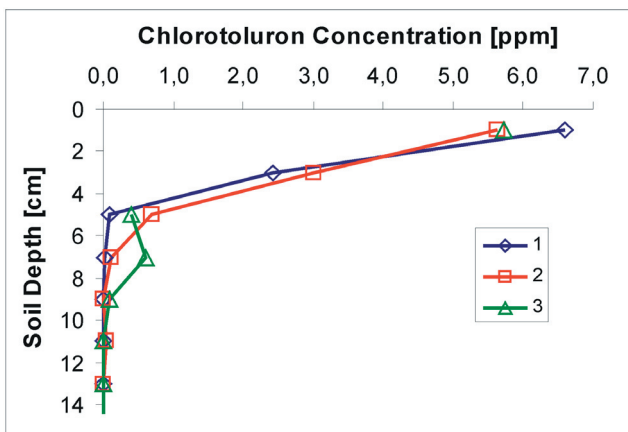


Fig. 13 Chlorotoluron concentrations detected in each sampling position in Dystric Cambisol in 2004 (A) and 2005 (B)

The total amounts of chlorotoluron within the monitored soil profiles on each sampling day are presented in Fig. 14. The results obtained 35 days after the application imply that the rate of chlorotoluron degradation at the beginning of the experiments was higher in 2005 than in 2004. On the basis of the climatic data it could be suggested that the chlorotoluron degradation rate would be similar in both years (with the exception of Haplic Phaeozem). The low chlorotoluron degradation rate in 2004 was probably caused by the fact that

the chlorotoluron applied on the plant surface in 2004 didn't degrade as quickly as the chlorotoluron applied on the soil surface in 2005. Due to this fact continuous disappearance of chlorotoluron in monitored soil units in 2004 was not found. Chlorotoluron, which is relatively stable to UV light (Tomlin, 2006), stuck to the plant leaves and was washed off the plant onto the soil surface during the experiment. Similar phenomenon of chlorotoluron behaviour was described by Zander et al. (1999). The other possible explanation

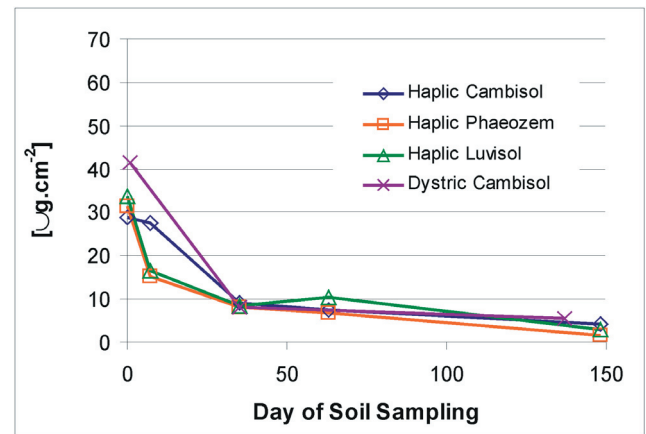
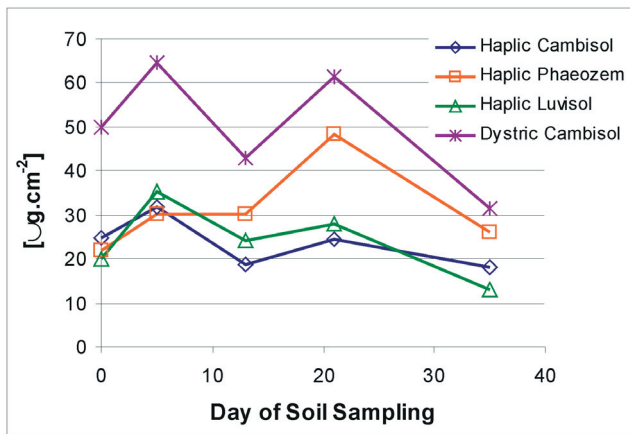


Fig. 14 Total amounts of chlorotoluron observed during the experiment in 2004 (A) and 2005 (B)

of the higher chlorotoluron degradation rate in 2004 could be that the mature growth, in which the chlorotoluron was applied, shaded the soil surface and thus decreased its temperature. The barley transpiration also caused soil moisture decrease. These two factors reduced the microbial degradation rate of chlorotoluron. Furthermore, the shaded soil surface also decreased the possibility of chlorotoluron photodegradation. And finally, the preferential flow could also lower the rate of degradation because of decreased microbial activity in subsurface horizon in Haplic Phaeozem.

The continuous disappearance of chlorotoluron in time was observed in 2005. The only exception occurred in Haplic Luvisol, where the total amount of chlorotoluron was slightly higher 63 days after application than it was 35 days after the application. In this case this effect was probably caused by the soil heterogeneity. Chlorotoluron can be concentrated in the convex places of the trial field. In addition, chlorotoluron can be transported in soil by the path deflected from the horizontal axis. Significantly higher total amount of chlorotoluron was found in Dystric Cambisol than in other soil units at the beginning of the experiments in both years. This observed fact was evident during all the sampling terms in 2004 as well. This was probably caused by the flow domain reduction due to high gravel content (32%) in this soil type.

The percentages of the remaining chlorotoluron in the soil profiles from the theoretically applied dose 35 five days after the herbicide application were 46.1 % in Haplic Luvisol, 65.0 % in Haplic Cambisol and 102.9 % in Haplic Phaeozem in 2004. As it was reported by KOČÁREK *et al.* (2005), the very high value obtained for Haplic Phaeozem was probably caused by the preferential flow, deviation of the solute flow from the vertical axes and low herbicide degradation rates in lower layers. The percentages of remaining chlorotoluron in the soil profile from the theoretically applied dose 35 days after herbicide application were 29.97 % in Haplic Luvisol, 30.78 % in Haplic Phaeozem and 38.58 % in Haplic Cambisol in 2005.

The persistence of chlorotoluron in 2004 was prolonged because of the post-emergent herbicide application.

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