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DEGRADATION RATE OF CHLORIDAZON IN SOIL AS INFLUENCED BY ADJUVANTS

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Abstract: The aim of this work was to evaluate the influence of an adjuvant addition on chloridazon degradation rate in soil. The experiment was carried out under controlled laboratory conditions. Chloridazon was applied alone and in a mixture with three different adjuvants: oil, surfactant and multicomponent (used for preemergence application). Chloridazon residue was analysed using gas chromatography with electron capture detector (GC/ECD). Good linearity was found between logarithmic concentration of chloridazon residues and time. The addition of oil and surfactant adjuvants slowed down the degradation of chloridazon in soil. The DT_{50} values for the mixture of chloridazon + oil and surfactant adjuvants was about 8–14 days higher in comparison with the DT_{50} for chloridazon applied alone (43 days). No significant differences were observed between degradation rates and the DT_{50} for chloridazon applied alone and with a multicomponent adjuvant.

Key words: chloridazon, adjuvant, degradation rate, herbicide residue, soil

INTRODUCTION

The first synthetic pesticides became available during the 1940s, generating large benefits in increased food production. Concern about the adverse impacts of pesticides on the environment and on animal and human health started to be voiced in the early 1960s. Since then, debate on the risks and benefits of pesticides has not ceased and a huge amount of research has been conducted into the impact of pesticides on the environment (van der Werf 1996).

The processes, as degradation by soil microorganisms, chemical degradation, sorption and binding by organic and mineral components, uptake by plant roots, and volatilization determine pesticide behaviour in soil. Modelling of field behaviour of pesticides started around 1970 (Leistra 1971; Walker 1974). Different kinetic models have been used to describe herbicide dissipation in soil. The models most often used in similar studies are: single first order, single second order and biexpotential kinetics such as Gustafson and Holden or first order multi-compartment (Vink *et al*. 1994; van der Pas *et al*. 1999; Diez and Barrado 2010). The modelling plays a major role in the assessment of pesticide behaviour in the environment, for registration at the EU level (Boesten 2000).

Chloridazon – 5-amino-4-chloro-2-phenylpyridazin-3(2*H*)-one, is the active substance (alone and in mixtures) of many herbicide products widely used for weed control in beet crops (Dexter and Zollinger 2001; Cuevas *et al*. 2007). This herbicide is applied pre- and post-emergence to control weeds, such as *Amaranthus retroflexus, Anthemis arvensis*, *Capsella bursa-pastoris*, *Chenopodium album*, *Fumaria officinalis*, *Galium aparine*, *Lamium* spp., *Solanum nigrum*, *Stellaria media*, *Thlaspi arvense* and *Veronica* spp. Chloridazon is rapidly absorbed by roots and translocated to all plant parts (Tomlin 2006).

The use of spray-tank adjuvants which improve the efficacy of foliar applied crop protection products, including post emergence herbicides, is well known and there are a great numbers of adjuvants available for that purpose in the market (Krogh *et al*. 2003; Foster *et al*. 2006). Properties of adjuvants increase herbicide activity through mechanisms such as droplet adhesion, retention, spreading, deposit formation, uptake and translocation. These adjuvant properties can be chemical, physical or biological in nature (Bruce and Carey 1996; Sharma *et al*. 1996). Only a few literature references report the effects of tank mix adjuvants on pre-emergence herbicides (McMullan *et al*. 1998). In practice, such combinations are seldom used because of the lack of consistent effects and the fact that most pesticide registrants do not recommend the use of a tank mix adjuvant on their labels. There is research that indicates adjuvants can reduce herbicide leaching through the soil profile (Reddy 1993). The listed properties of adjuvants can influence the concentration of herbicide residues in the soil. Adjuvants strongly influence pesticide delivery, uptake, redistribution, persistence and thus, the final biological performance (Krogh *et al*. 2003; Cabrera *et al*. 2010).

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The aim of this work was to evaluate the influence of an adjuvant addition on the chloridazon degradation rate in soil.

MATERIALS AND METHODS

The influence of an adjuvant addition on the degradation rate of chloridazon was studied under controlled laboratory conditions. The soil (black soil; pH = 6.3; organic carbon content = 2.01%; sand, silt and clay content = 15, 34 and 51%, respectively) was collected for the laboratory experiments from the upper layer (0–15 cm). The soil had no history of previous chloridazon use (residues were not detected) and this soil was representative of the beet-growing regions of Lower Silesia (South-west Poland).

After passing the soil through a 2-mm sieve, it was stored in covered trays in a greenhouse for 10 days and regularly mixed. Soil moisture was measured before the start of the trials by heating the soil until it was dry for 24 h at 105°C and then determining the difference in weight. Soil moisture was set at 60% of field capacity, checked at regular intervals, and adjusted with distilled water to the initial level.

Soil samples were transferred into pots with a 90 mm diameter and 85 mm height. Pots were placed in growth chambers. Each variant had four replicates. Day/night temperature regimes were 18/9°C (average temperatures recorded in the second part of April and May – the typical term of chloridazon application in field in Poland). Light intensity was 320±10 μmol/m^2/s photosynthetic photon flux, with a 15 h day length.

Two days after placing the pots into the growth chambers, the commercial formulation of chloridazon (herbicide Pyramin 65 WP) at 1,950 g of active substance per ha, was applied alone and in a mixture with three different adjuvants: Olemix 84 EC (mineral oil SAE 10/95) at 1.5 l/ha, Trend 90 EC (ethoxylated isodecyl alcohol - surfactant) at 0.3 l/ha and BackRow (multicomponent adjuvant) – at 0.3 l/ha. BackRow adjuvant based on a blend of nonionic surfactants, emulsifiers, sticking agents, and selected oils is specifically designed for pre-emergence herbicides (producer's information). Application of the herbicide and adjuvants was done using a stationary chamber sprayer equipped with a mobile nozzle TeeJet XR 11003-VS. The nozzle was operated at a pressure of 200 kPa and speed 2.5 km/h producing a spray volume of 250 l/ha. The dose of the herbicide, the adjuvants and the spraying conditions were the same as for field conditions.

Soil samples (one pot containing ca. 250 g of soil = one sample and one replication) were taken for analyses after 1 hour (initial concentration) and then on day 4, 16, 32, 48, 64, 80, 96, 112 and 128 days after treatment (DAT).

Samples taken for the experiment were well mixed and stored in polyethylene bags at minus 20°C until extraction. The analytical procedure consisted of three elementary processes: extraction of the analyzed substance from the matrix (methanol through 24 h), cleaning of the extract using SPE (Solid Phase Extraction) column with C18 active solid, and final determination using gas chromatography (Varian, CP 3800) equipped with an electron capture detector (ECD) and VF–5MS capillary column (30 m length x 0.25 mm diameter). The recovery of the chloridazon was determined by fortification of soil samples at concentrations of 0.001, 0.01, 0.1 and 1.0 mg/kg in three replicates. The average recovery for all concentrations was 97%. The quantification limit of the method was 0.001 mg/kg for 20 g of soil sample.

The degradation kinetics of the chloridazon in soil were determined by plotting the residue concentration against time. The maximum squares of the correlation coefficients (R^2) found were used to determine the equations of best fit curves. The rate equation was calculated from the first order rate equation: $C_t = C_0 e^{-kt}$, where C_t represents the concentration of the herbicide at time t, C_0 represents the initial concentration and k is the rate constant. The rate of degradation is characterised by a half-life (DT_{50} – dissipation time for 50% of the initial residue to be lost). The DT_{50} values were graphically derived by interpolating the values between successive residue measurements, and calculated from equations. All experimental data were calculated using the statistical program Statgraphics Centurion, version XV and Excel (MS Office 2000).

RESULTS AND DISCUSSION

The result of the chloridazon degradation rate in surface soil is shown in figure 1. The initial chloridazon concentration 1 hour after application for all samples amounted to 1.034±0.031 mg/kg. At 128 DAT, chloridazon residue in soil decreased to 0.074 mg/kg (7.2% of initial dose). The degradation data were plotted. Good linearity was found between logarithmic concentration of chloridazon residues and time, indicating first-order rates of degradation with a correlation coefficient (R^2) of about 0.98. The DT_{50} value (graphically derived by interpolating the values between successive residue measurements) amounted to 43 days. Whereas the DT_{50} value obtained after fitting the curve to first-order kinetics was lower (35 days); (Table 1). The same model of the kinetics equation has been noticed for other herbicides (Pettygrove and Naylor 1985; Allen and Walker 1988; Ravelli *et al*. 1997; Cuevas *et al*. 2007). The DT_{50} values for soil in this experiment, are from the data of Tomlin (2006). The DT_{50} found for chloridazon in the literature varied from 8 up to 104 days (Fan de Fang *et al*. 1983; Pestemer and Malkomes 1983; Capri *et al*. 1995; Rouchaud *et al*. 1997). The high values of DT_{50} indicate that chloridazon is a persistent substance in soil. Capri *et al*. (1995) found a high persistence and low mobility of chloridazon in silty clay loam soil in northern Italy. Russo *et al*. (1993) found no traces of chloridazon in groundwater samples collected in the same area.

Based on the degradation data concerning treatments where herbicides were applied with adjuvants, good linearity was also found between the logarithmic concentration of chloridazon residues and the time; the correlation coefficient was about 0.98–0.99. The degradation pattern differed significantly between chloridazon alone, and in a mixture with oil and surfactant adjuvant. The addition of oil and surfactant reduced the degradation rate of chloridazon in soil (Fig. 1). No significant differences were observed between degradation rates for chloridazon applied alone and with a multi-component adjuvant.

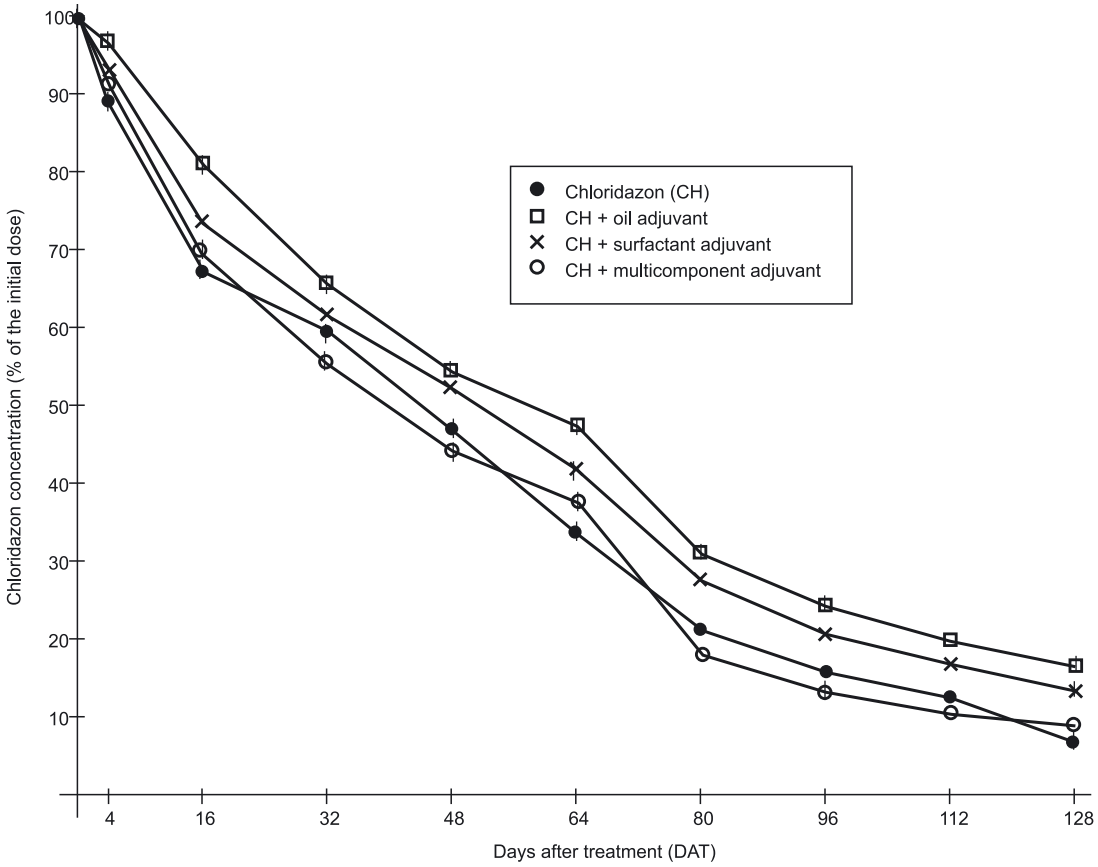

Fig. 1. Degradation of chloridazon in soil. Vertical bars represent ± standard errors of the mean (n = 4)

Table 1. Equations for chloridazon degradation curves and values of DT_{50}

Object	Equation of degradation curve (for average values)	DT_{50} [days]	
		graphically determined	calculated from equation
Chloridazon (CH)	$C_t = 1.071 \times e^{-0.0195 \times t}$, $R^2 = 0.984$	43.45±2.15	35.54
CH + oil adjuvant	$C_t = 1.070 \times e^{-0.0144 \times t}$, $R^2 = 0.990$	57.36±3.24	48.13
CH + surfactant	$C_t = 1.046 \times e^{-0.0157 \times t}$, $R^2 = 0.991$	51.04±2.96	44.17
CH + multicomponent adjuvant	$C_t = 1.056 \times e^{-0.0196 \times t}$, $R^2 = 0.979$	40.14±2.48	35.36

C_t – chloridazon concentration at time t, R^2 – correlation coefficient

The DT_{50} values for the mixture chloridazon + oil and surfactant were about 8–14 days higher than the DT_{50} values for chloridazon applied alone. The same differences were observed for data calculated from equations (Table 1). Final residues of chloridazon (128 DAT) in oil and surfactant adjuvant treatments were higher (0.151 and 0.180 mg/kg, respectively) than on treatments, where chloridazon was used alone. The DT_{50} values for the chloridazon + multicomponent adjuvant mixture were about 3 days shorter in comparison with DT_{50} for chloridazon applied alone. Whereas for data calculated from equations, the differences between values of DT_{50} were not observed (Table 1).

Adjuvants used in the formulation of the herbicide can change the agronomic effects of the formulated product (Pannacci *et al*. 2010). Adjuvants may also affect the environmental impact, as dispersion patterns may be altered and the functional activity period of the active substance may be lengthened or its degradation delayed (Levitan *et al*. 1995; van der Werf 1996; Swarcewicz *et al*. 1998). Unfortunately, very little information on the effects and fate of adjuvants is available in scientific literature. Mata-Sandoval *et al*. (2001) and Rodriguez-Cruz *et al*. (2007) noted that herbicides such as atrazine and linuron, degraded at a lower rate and to a lower extent in the presence of a surfactant. Earlier experiments conducted by authors (Kucharski and Sadowski 2009a, 2009b), also proved that the addition of adjuvants increased DT_{50} values and the level of herbicide active substances in soil. However, usually adjuvants are applied with herbicides at reduced doses (70–80% of recommended). Herbicidal residues determined at harvest time are lower than the residues obtained from a treatment, where recommended doses of herbicide without adjuvant were applied (Kucharski 2003).

CONCLUSION

Laboratory experiments show that good linearity was found between the logarithmic concentration of chlorida-

zon residues and time. Adding an adjuvant, especially an oil adjuvant, to a spray mixture slowed down the degradation rate and increased chloridazon residue in the top soil layer.

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