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Influence of adjuvants addition on lenacil residues in plant and soil

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Abstract. The aim of this work was to evaluate the influence of an adjuvant addition on lenacil residues in soil and roots of sugar beet. Field experiments were conducted during a three-year-period from 2008 until 2010 on arable fields located in southwestern Poland. Chemical weed control in sugar beet was carried by commercial formulation of lenacil. Herbicide was applied alone (recommended and reduced doses) and in mixture with adjuvants (oil, surfactant and multicomponent). Lenacil residue was analysed using HPLC/UV. At lifting time the residues of lenacil in soil amounted to 0.0006–0.0042 mg kg^{-1}. In sugar beet roots samples, the residues of lenacil were lower than in soil and amounted to <0.0005–0.0020 mg kg^{-1}. The addition of adjuvants caused an increase of the active substance residues in soil and roots of sugar beet in comparison with the treatments, where lenacil was used without adjuvant (reduced dose). The increase of the lenacil residues was statistically significant for most of soil and plant samples and amounted average to 45 and 41% respectively. Influence of single adjuvant on lenacil residues in soil and plant was different for each year (experimental season). The residues of lenacil determined in roots of sugar beet did not exceed acceptable value (MLR).

key words: adjuvant, herbicide, residue, lenacil, soil, sugar beet

INTRODUCTION

Each year above million tons of herbicides, insecticides, fungicides and other pesticides are applied to agricultural crops worldwide. The amount of pesticide coming in direct contact with or consumed by target pests is an extremely small percentage of the amount applied. In most studies the proportion of pesticides applied reaching the target pest has been found to be less than 0.3%, so 99.7% went to the environment (Pimentel, 1995). Since the use of pesticides in agriculture inevitably leads to exposure of non-target organisms (including humans), undesirable side effects may occur on some species, communities or on ecosystems as a whole (Van der Werf, 1996).

Monitoring of herbicide residues allows controlling the quality of agricultural products and contamination of soils. The results from monitoring studies need to be compared to the acceptable amounts of the EU-standards. The standards define maximum residue limits for different active ingredients and plant products. Information on the residue and degradation rate of herbicides allows evaluating the behavior of herbicides in the environment.

Lenacil – 3-cyclohexyl-1,5,6,7-tetrahydrocyclopentapyrimidine-2,4(*3H*)-dione (IUPAC) is the active substance (alone and in mixtures) of many herbicide products widely used to control weeds in beet crops (Dexter and Zollinger, 2001; Cuevas et al., 2007). Lenacil, as herbicide is applied pre- and post-emergency to control weeds, such as *Capsella bursa-pastoris, Lamium amplexicaule*, *Veronica persica*, *Anthemis arvensis, Viola arvensis, Polygonum convolvulus, Brassica napus, Papaver rhoeas* and *Chenopodium album*. Lenacil is 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 great numbers of adjuvants available for that purpose in the market (Krogh et al., 2003; Foster et al., 2006). Properties of adjuvant increased 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 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 pes-

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ticide registrants do not recommend the use of a tank mix adjuvant on their labels. Some research indicates that adjuvants can reduce leaching of herbicide through the soil profile (Reddy, 1993). The listed properties of adjuvants can influence the concentration of herbicide residues in soil. Adjuvants strongly influence pesticide delivery, uptake, redistribution, persistence and thus the final biological performance (Krogh et al., 2003; Cabrera et al., 2010).

The aim of this work was to evaluate the influence of three adjuvants addition on lenacil residues in soil and roots of sugar beet.

MATERIAL AND METHODS

Field experiment

Field experiments were conducted during a three-year-period from 2008 until 2010 on arable fields located in southwestern Poland (black soil, pH = 6.1–6.5, organic carbon content 2.04–2.13% and clay content 45–52%). The field trial was set up as a randomized complete block design with four replicates. All farming activities were carried out in accordance with conventional agricultural practice and in line with recommendations from officials. Chemical weed control in sugar beet was carried by commercial formulation of lenacil (Venzar 80 WP, DuPont de Nemours) at the doses 800 and 600 g of active substance per ha (recommended and reduced doses respectively). Herbicide was applied alone (in both doses) and in mixture (reduced dose) with three different adjuvants: Atplus 60 EC (paraffin oil) in the rate 1.5 l ha^{-1} – oil adjuvant, Break Thru S 240 (polymethylsiloxane copolymer) in the rate 0.3 l ha^{-1} – surfactant adjuvant and BackRow (multicomponent adjuvant) – in the rate 0.3 l ha^{-1}. BackRow adjuvant based on a blend of non-ionic surfactants, emulsifiers, sticking agents and specialist oils has been specifically designed to optimize coverage and desorption of pre-emergence herbicides onto the soil surface (producer's information). Herbicide and its mixtures were applied pre-emergency after sugar beet sowing (in the third decade of April).

The effect of herbicide and adjuvant application on residues in plant and soil profile was studied. Samples of soil and roots of sugar beet were taken at the day of lifting (in the first decade of October – 159–166 days after treatment). The samples were taken from the middle of each plot to avoid interference and side effects from the neighboring plots. The soil samples were taken at the top soil layer (0–15 cm of depth).

In years 2008–2010 weather conditions, especially rainfalls, from April to July (for 3 months after herbicide treatment), the most deviated from average conditions in this region of Poland (recorded from 1961 to 2000); (Table 1).

Table 1. Average rainfalls recorded in southwest Poland.

Year	Average rainfall [mm]			
	April	May	June	July
2008	55.1	40.7	29.3	44.2
2009	24.7	65.7	180.8	145.1
2010	50.6	136.8	49.4	116.8
(1961–2000)	37.6	61.3	71.4	80.0

Analytical procedure of lenacil determination

Samples taken from experiments were well mixed and stored in polyethylene bags at minus 20^{o}C until sample extraction. The analytical procedure consisted of three elementary processes: extraction of analyzed substance from matrix (using Extractor DIONEX ASE 350, extraction solvent – methanol), cleaning of extract using SPE (Solid Phase Extraction) column with C18 active solid and final determination using high performance liquid chromatography (SHIMADZU HPLC measuring set: pump LC-10AT, degasser DGU-4A) with UV-detection (SPD-10A). The separation of compounds was performed using a HyperClone ODS C18 (4.6 x 250 mm) column and 50% of acetonitrile + 40% of water + 10% of methanol (V/V) as mobile phase at a flow rate 0.4 ml min^{-1}. The injection volume was 20 μl and detection was performed at 230 nm. The recovery of the lenacil was determined by fortification of soil samples at concentrations of 0.001, 0.01, 0.1 and 1.0 mg kg^{-1} in three replicates. The average recovery for all concentrations was 96% for soil and 92% for plant. The quantification limit of the method was 0.0005 mg kg^{-1} for 30 g of soil and plant samples. Analytical procedures were performed at the Institute in Laboratory of Residue Research. This method based on procedure described in Polish Standard (PN-R-04121, 1997).

All experimental data were calculated using the statistical program Statgraphics Centurion, version XV.

RESULTS

At lifting time, in soil samples taken from plots, the residues of lenacil amounted to 0.0006–0.0042 mg kg^{-1}. In sugar beet roots samples, the residues of lenacil were lower than in soil and amounted to <0.0005–0.0020 mg kg^{-1}. The level of residues was dependent on the dosage of substance, addition of adjuvant and weather condition in individual vegetation seasons. Results obtained from all experiments are shown in Table 2. The addition of adjuvants caused an increase of the active substance residues in soil and roots of sugar beet in comparison with the treatments, where lenacil was used without adjuvant (reduced dose). The increase of the lenacil residues was statistically significant for most of soil and plant samples and amounted average to 45 and 41% respectively. Influence of single adjuvant on lenacil residues in soil

Table 2. Residues of lenacil in soil and roots of sugar beet.

Object	Residues# [mg kg^{-1}]					
	2008		2009		2010	
	soil	root	soil	root	soil	root
Lenacil (FD)	0.0042	0.0020	0.0026	0.0011	0.0015	0.0006
Lenacil (RD)	0.0023	0.0009	0.0012	0.0006	0.0006	ND
Lenacil (RD) + A1	0.0034	0.0015	0.0015	0.0009	0.0011	0.0005
Lenacil (RD) + A2	0.0031	0.0012	0.0020	0.0007	0.0009	ND
Lenacil (RD) + A3	0.0033	0.0014	0.0019	0.0008	0.0008	ND
LSD(0.05)	0.00072	0.00028	0.00067	0.00012	0.00021	-

average residues for 4 replications
FD – full (recommended) dose; RD – reduced dose
A1 – oil adjuvant; A2 – surfactant adjuvant, A3 – multicomponent adjuvant
ND – residue did not detect (<0.0005 mg kg^{-1})

and plant was different for each year (experimental season). The residues of lenacil determined in roots of sugar beet did not exceed acceptable value – MRL (Maximum Residue Levels for roots of sugar beet = 0.1 mg kg^{-1}); (EC/839/2008).

DISCUSSION

The residues level detected in soil and sugar beet roots was different in each vegetation season. In this period the residues level was strongly affected by rainfalls occurring after herbicide application. In 2008, the average rainfalls from April to July amounted to 169.3 mm and were lower than for long-term observations (250.3 mm); (Tab. 1). The two next years were wetter – the average rainfalls amounted to 416.3 and 353.6 mm respectively. An increase of rainfalls influence the leaching herbicide into soil profile (substance moves to deeper soil layer) and residues detected in the top soil layer and plants are lower (Cuevas et al., 2007). This effect was more evident when intensive rainfalls occurred at first weeks after treatment (year 2010).

The DT_{50} (dissipation time for 50% of the initial residue to be lost) found for lenacil in the literature are very variable, from 32 up to 125 days (Tena et al., 1982; Zhang et al., 1999; Cuevas et al., 2007). The high values of DT_{50} indicate, that lenacil belongs to substances of elevated persistence in soil. Cuevas et al. (2007) found a high persistence and low mobility of lenacil in a clayey soil in southwest Spain, where lenacil residues in top layer were still detected 60 days after herbicide application.

A pesticide must be intrinsically very active and be able to express that high activity under a range of commercially acceptable delivery systems and environmental conditions. Adjuvants help pesticides express this activity and their effectiveness depends on their physicochemical properties (Pannacci et al., 2010). Influence of adjuvants on herbicide residues in soil and plant, degradation rate and leaching depend on the kind of adjuvant (Kucharski and Sadowski, 2009b). Swarcewicz et al. (1998) described experiments where influence of adjuvants on trifluralin degradation was tested in green house conditions. At 50 days after treatment residues of trifluralin amounted to 38% of the initial dose and on treatments with adjuvants residues ranged from 42 to 49% of the initial dose. Similar experiment conducted in the green house condition (Kucharski and Sadowski, 2009a) also proved that the addition of oil adjuvant slowed down degradation and increased the level of ethofumesate residue in soil. The DT_{50} value for the mixture of ethofumesate + adjuvant was about 8–10 days higher in comparison with the DT_{50} for ethofumesate applied alone. The effect of organic additives, especially oil substances, on increase of herbicide retention, mobility and immobilization in soil top layer was described by other authors (Koskinen et al., 2006; Todoruk and Langford, 2006; Kaushik and Neera, 2007; Cao et al., 2008). This study and cited references inform that the addition of adjuvants could influence speed of degradation and increase herbicide residues in soil and plant, but usually adjuvants are applied with herbicides in reduced doses (70–80% of recommended) and herbicidal residues determined at harvest time are lower than those obtained from treatments, where full (recommended) doses of herbicide (without adjuvant) were applied (Kucharski, 2003).

CONCLUSION

Addition of adjuvants influenced the increase of lenacil residues in the top soil layer and roots of sugar beet. The increase of the lenacil residues was statistically significant for most of soil and plant samples and amounted to 43% (average) in comparison with the objects, where lenacil was used without adjuvant. Influence of single adjuvant on lenacil residues in soil and plant was different for each year (experimental season). The residues of lenacil determined in roots of sugar beet did not exceed acceptable value (MRL).

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