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Influence of adjuvants on behavior of phenmedipham in plant and soil

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Abstract. The aim of the present study was to determine the influence of an addition of adjuvants on behaviour of phenmedipham in agricultural environment – residues in soil, plant, degradation rate and leaching into the soil profile. Field experiments were conducted during a three-year-period from 2006 until 2008 on arable fields located in South-Western Poland. Chemical weed control in sugar beet was carried out by commercial formulation of phenmedipham. The herbicide was applied alone and in mixture with adjuvants (oil and surfactant). Phenmedipham residues were analysed using high performance liquid chromatography with UV detection. At lifting time, in soil samples taken from plots where phenmedipham was applied alone, the residues amounted to 0.0082–0.0128 mg kg^{-1}. In sugar beet roots samples, the residues of phenmedipham were lower than in soil and amounted to 0.0032–0.0084 mg kg^{-1}. The addition of adjuvants caused an increase of the active substance (a.s.) residues in soil and roots of sugar beet. The residues of phenmedipham determined in roots did not exceed acceptable values MRLs (Maximum Residue Levels). The addition of oil adjuvant reduced the degradation rate of phenmedipham in soil. No significant differences were observed between degradation rates for phenmedipham applied alone and with surfactant adjuvant. The DT_{50} value for mixture phenmedipham + oil adjuvant was about 11 days higher in comparison with DT_{50} for phenmedipham applied alone and amounted 32.1 (±2.1) days. Addition of adjuvants, especially oil adjuvant, to herbicide caused the slowdown of phenmedipham leaching into soil profile.

key words: adjuvant, degradation rate, herbicide, leaching, phenmedipham, residues

INTRODUCTION

Phenmedipham [methyl 3-(3-methylcarbaniloyloxy) carbanilate] is the active substance (alone and in mixtures) of many herbicides widely used for weed control in beet crops (Dexter, 1994; Dexter, Zollinger, 2001; May, 1996). In Poland, phenmedipham is registered for control of broad-leaved weeds, as: *Sinapis arvensis, Stellaria media, Thlaspi arvense, Galinsoga parviflora, Senecio vulgaris* and *Lamium* spp. in strawberries, red and sugar beet (Domaradzki, 2007). Phenmedipham is absorbed through the leaves with translocation primarily in the apoplast. This active ingredient of herbicides does not accumulate in soil, nor is there any relevant uptake by following crops. DT_{50} in soil amounts to an average of 25 days (Tomlin, 2006).

Herbicides are often applied at rates higher than required for weed control under ideal conditions. This is done primarily to compensate losses that occur at the target site in the plant (McMullan et al., 1998). In soils, the biological activity of herbicides may be decreased by chemical or biological degradation of active ingredients. Adsorption by soil colloids, absorption by plants or leaching to lower layers of the soil profile influences also the biological activity of herbicides in the soil (Harris, 1969). In plants, the biological activity of herbicides may by decreased by low retention and washing of herbicide from leaves surface by rain, dew and irrigation to the soil (Nalewaja et al., 1995). Numerous research studies show that adjuvants applied with herbicide influenced weed control efficacy (Knoche, 1994; 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). 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 plant and soil.

In the USA and Europe there is no official definition of „what is adjuvant". The Weed Science Society of America states that adjuvant is any substance in a herbicide formulation or added to the spray tank to modify biological activity or application characteristics.

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A new 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. The advantages of even the best pesticides can be lost if it is applied with the wrong adjuvant. Adjuvants strongly influence pesticide delivery, uptake, redistribution, persistence and thus the final biological performance.

The aim of the present study was to determine the influence of an adjuvants addition on behavior of phenmedipham in agricultural environment – residues in soil, plant, degradation rate and leaching into the soil profile.

MATERIAL AND METHODS

Field experiments were conducted during a three-year-period from 2006 until 2008 on arable fields located in South-Western Poland (brown soils, pH = 6.1–6.5, organic carbon content 2.04–2.24% and clay content 45–56%). 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 phenmedipham (herbicide Betanal 160 EC) at the dose 960 g ha^{-1}. Herbicide was applied alone and in mixture with adjuvants: Atpolan Bio 80 EC (methylated esters of fatty acids from rape oil) in the dose of 1.5 l ha^{-1} and Break Thru 240 EC (polymethylsiloxane copolymer surfactant) in the dose of 0.3 l ha^{-1}. Herbicide and its mixtures were applied postemergence at 2–4 leaf weed stage.

Samples of soil and roots of sugar beet were taken at the day of lifting. The samples were taken from the middle of each plot to avoid interference and side effects from the neighbouring plots. The soil samples were taken at a soil depth of 0–15 cm.

The influence of adjuvants addition on degradation rate of phenmedipham was studied in 2007 only. Soil samples from the same plots were taken to analyses at 1 hour (initial concentration) and 3, 12, 21, 36, 54, 72, 90, 120 and 150 days after treatment (DAT).

Additionally in the 2007 the effect of herbicide and adjuvants application on mobility of phenmedipham into soil profile was studied. The samples of soil were taken at 6, 12 and 20 (lifting time) weeks after the application of herbicide and its mixtures with adjuvants from three soil layers (0–15, 16–30 and 31–50 cm).

Samples taken from each experiment were well mixed and stored in polyethylene bags at minus 20 ^{o}C until sample extraction. Soil moisture content was determined for each soil sample. The samples were dried out at 105 ^{0}C for 24 h. Phenmedipham residue was analysed using high performance liquid chromatography (SHIMADZU HPLC measuring set: pump LC-10AT, degasser DGU-4A) with UV-detection (SPD-10A). The recovery of the phenmedipham was determined by fortification of soil and root samples at concentrations of 0.0001, 0.001, 0.01 and 0.1 mg kg^{-1} in three replicates. The average recoveries for all concentration were 86% (soil) and 78% (roots of sugar beet). The quantification limit of the method was 0.0001 mg kg^{-1} for both kinds of sample. The analytical procedure was performed at the Institute and described by authors (Kucharski, 2007). All experimental data were calculated using the statistical program Statgraphics Centurion, version XV.

RESULTS

Residues in plant and soil

At lifting time, in soil samples taken from plots where phenmedipham was applied alone, the residues amounted to 0.0082–0.0128 mg kg^{-1}. In sugar beet roots samples, the residues of phenmedipham were lower than in soil and amounted to 0.0032–0.0084 mg kg^{-1} (Table 1). The addition of adjuvants caused an increase of the active substance (a.s.) residues in soil and roots of sugar beet in comparison with the treatments where phenmedipham was used without adjuvants. The increase of the herbicide a.s. residues was statistically significant for 50% of soil samples (only for oil adjuvants) and 66% of sugar beet root samples.

Table 1. Residues of phenmedipham in soil and roots of sugar beet.

Treatment#	Phenmedipham residues (average values for 4 replications) [mg kg^{-1}]					
	2006		2007		2008	
	soil	roots	soil	roots	soil	roots
H	0.0128	0.0084	0.0106	0.0063	0.0082	0.0032
H + O	0.0145	0.0103	0.0136	0.0069	0.0109	0.0050
H + S	0.0132	0.0097	0.0114	0.0076	0.0095	0.0036
LSD(0.05)	0.00127	0.00110	0.00183	0.00012	0.00172	0.00164

H – herbicide, O – oil adjuvant, S – surfactant adjuvant.

The residues of phenmedipham determined in roots of sugar beet did not exceed acceptable values (0.1 mg kg^{-1}); (EC/839/2008).

Degradation rate in soil

The degradation data were plotted. Good linearity was found between logarithmic concentration of phenmedipham residues and time, indicating first-order rates of degradation with correlation coefficients (r^2) about 0.96–0.98.

The DT_{50} values (graphically derived by interpolating the values between successive residue measurements) amounted 21.4 (±2.1) days for soil (phenmedipham applied alone). The results of the phenmedipham degradation in soil and influence of adjuvants are shown in Fig. 1.

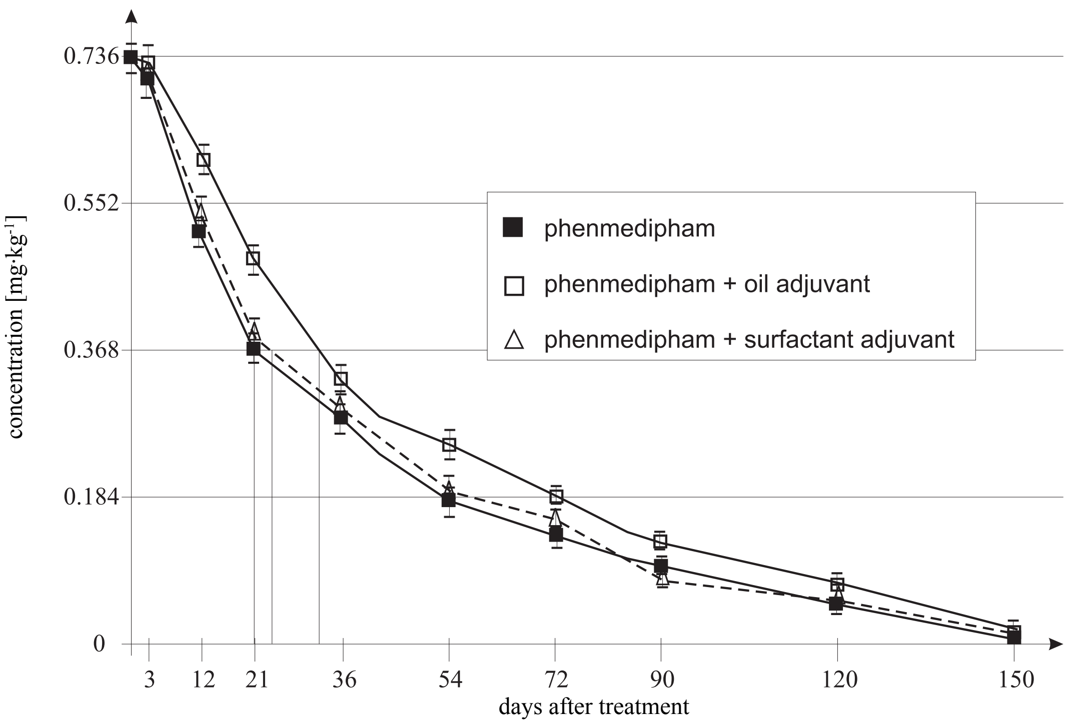

Fig. 1. Phenmedipham degradation in soil. Vertical bars represent ± standard errors of means (n = 4). Bars where not present fall within the symbols.

The degradation pattern differed significantly among the treatments: phenmedipham alone and in mixture with oil adjuvant. The addition of oil adjuvant reduced the degradation rate of phenmedipham in soil. No significant differences were observed between degradation rates for phenmedipham applied alone and with surfactant adjuvant. The DT_{50} value for mixture phenmedipham + oil adjuvant was about 11 days higher in comparison with DT_{50} for phenmedipham applied alone and amounted 32.1 (±2.1) days. Final residues of phenmedipham in 2007 are shown in Table 1. No significant differences were observed between DT_{50} and final residue level for phenmedipham applied alone and with surfactant adjuvant. The DT_{50} value for mixture phenmedipham + surfactant amounted 23.2 (±2.3) days.

Table 2. Residues of phenmedipham in soil layers.

Soil layer [cm]	Phenmedipham residues [mg kg^{-1}]			
	without adjuvant	with oil adjuvant	with surfactant adjuvant	$LSD_{0.05}$
Sampling 6 weeks after herbicide application				
0–15	0.2415	0.2986	0.2504	0.03827
16–30	0.0218	0.0174	0.0208	0.00281
31–50	0.0002	ND	ND	-
Sampling 12 weeks after herbicide application				
0–15	0.1141	0.1413	0.1196	0.02141
16–30	0.0032	0.0012	0.0026	0.00152
31–50	0.0006	0.0001	0.0004	0.00012
Sampling 20 weeks after herbicide application				
0–15	0.0106	0.0136	0.0114	0.00183
16–30	0.0009	0.0014	0.0011	0.00029
31–50	0.0011	ND	0.0008	0.00046

ND – residues not detected (<0.0001 mg kg^{-1}).

Leaching into soil profile

The addition of oil adjuvant caused an increase of the phenmedipham residues in surface layer of soil (0–15 cm). Moreover, the oil adjuvant addition caused that speed of leaching of herbicide a.s. into soil profile was slower than in the treatments where herbicide was applied alone. At lifting time the phenmedipham residue in the deepest soil layer (31–50 cm) amounted 0.0011 mg kg^{-1} for treatments without adjuvant, and no residue was detected (<0.0001 mg kg^{-1}) for the treatment where herbicide was applied with oil adjuvant (Table 2). For samples with surfactant adjuvant significant differences between treatments (with and without adjuvant) were not observed.

DISCUSSION

Influence of adjuvants on herbicide residues in soil and plant, degradation and leaching depend on the kind of adjuvant. Significant differences in degradation rate of the herbicide in soil in the first period after treatment influenced the DT_{50} indicator. The DT_{50} values for soil are consistent with the data of Tomlin (2006) – average DT_{50} value in soil for different experiments amounted ca. 25 days. The DT_{50} values for phenmedipham obtained from a greenhouse experiment was lower and ranged from 9 to 15 days (Kucharski 2004). The addition of oil adjuvant slowed down the degradation of phenmedipham in soil and increased the level of residue in soil and plant. Swarcewicz et al. (1998) described experiments where influence of adjuvants on trifluralin degradation was tested in greenhouse conditions. At 50 DAT 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 greenhouse conditions (Kucharski, Sadowski, 2009) 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 were described by other authors (Jun et al., 2008; Kaushik, Neera, 2007; Koskinen et al., 2006; Todoruk, Langford, 2006). In these experiments there were no significant differences between DT_{50} and residue level for phenmedipham applied alone and with surfactant adjuvant. In a study conducted by Rodriguez-Cruz et al. (2007) leaching of linuron and atrazine compounds was studied in columns of a natural clayey soil and in the same clayey soil modified by direct injection of the surfactant. Breakthrough curves indicated the total immobilization of these substances in modified soils and a decrease in the leaching kinetics compared to what was obtained in the natural soil. This study and the cited references inform that the addition of adjuvants, especially oil adjuvants, could influence speed of degradation and increase herbicide residues in soil, 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 the treatments where full (recommended) doses of herbicide (without adjuvant) were applied (Kucharski, 2003).

CONCLUSION

Addition of adjuvants, especially oil adjuvant, to herbicide caused slowdown of the degradation rate and leaching of phenmedipham into soil profile. Moreover the addition of adjuvant increased the content of phenmedipham residues in the top soil layer and roots of sugar beet.

The residues of phenmedipham determined in roots of sugar beet did not exceed acceptable values MRLs (Maximum Residue Levels).

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