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Impact of adjuvants on: phenmedipham, desmedipham and ethofumesate residues in soil and plant

Mariusz KUCHARSKI

Institute of Soil Science and Plant Cultivation, National Research Institute,
Dept. of Weed Science and Tillage Systems
St. Orzechowa 61, 50-540 Wrocław, Poland
e-mail: m.kucharski@iung.wroclaw.pl

Abstract: The aim of investigations was to evaluate the influence of herbicides and adjuvant application on residues in soil and plant material. Field experiments were carried out during 2003-2005 on arable field localized in South-West Poland. Herbicidal preparation to control weeds in sugar beet (containing phenmedipham, desmedipham and ethofumesate), was applied at recommended dose, reduced dose and at reduced dose in mixture with three different adjuvants (mineral oil, plant oil and surfactant). Samples of soil and roots of sugar beet were taken on the day at sugar beet lifting. Herbicide residues in all samples were determined using high performance liquid chromatography with UV-detection. The highest concentration of herbicide active substances were determined in samples from field plots, where herbicidal preparation was applied at full (recommended) dose. Reduction of herbicide dose caused a decrease of residues. The addition of adjuvants caused an increase of the herbicide active substance residue in the soil and roots of sugar beet comparing plots with a reduced dose of preparation without adjuvants added. Residues of active substances determined in roots of sugar beet did not exceed EU acceptable limits.

Keywords: herbicide, adjuvant, residue, sugar beet

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 human health started being voiced in the early 1960s. Since then, debate on the risk and benefits of pesticides has not ceased and a huge amount of research has been conducted into the impact of pesticides on the environment [1].

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. Low soil and plant residues of herbicide constitute problems for their determination and make it difficult to estimate the effect of these herbicides on following crops and health of consumers [2].

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 [3]. 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 [4]. In plants, the biological activity of herbicides may be decreased by low retention and washing of herbicide from leaves surface by rain, dew and irrigation to the soil [5]. Numerous research studies show that adjuvants applied with herbicide influenced weed control efficacy [6]. Properties of adjuvant increased herbicide activity through mechanisms such as droplet adhesion, retention, spreading, deposit formation, uptake and translocation [7, 8]. Some research indicate that adjuvants can reduce leaching of herbicide through the soil profile [9]. The listed properties of adjuvants can influence the concentration of herbicide residues in plant and soil.

The aim of present investigation was to evaluate the influence of adjuvant application on herbicide residues in soil and roots of sugar beet.

MATERIALS AND METHODS

Field experiments were conducted during a three-year-period from 2003 until 2005 on arable fields localized in South-West Poland. 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 applied at recommended and reduced doses alone and at reduced dose in mixture with three different adjuvants: Olemix 84 EC, Z.Ch. Organika-Azot; Actirob 842 EC, Novance and Break Thru S-240, Goldschmidt – see Table 1. Herbicide and its mixtures with adjuvant were applied single at the stage of 2-4 leaves of beet. Betanal Progress AM 180EC (Bayer Crop Science) contains 3 active substances: phenmedipham, desmedipham and ethofumesate. The rates of active ingredients of the herbicidal preparation applied in experiments are given in Table 2.

Table 1. Characteristics of adjuvants used in experiments

Common name of adjuvant	Active substance	Dose [l ha^{-1}]
Olemix 84 EC	mineral oil SAE 10/95	1.5
Actirob 842 EC	methylated fatty acids from rape seed oil	1.5
Break Thru S-240	polymethylsiloxane copolymer	0.25

Table 2. The rate of herbicide active ingredient applied in experiments

Active substance (a.s.) of herbicidal preparation	IUPAC name	Dose a.s. [g ha^{-1}]	
		recommended	reduced
phenmedipham	methyl 3-(3-methylcarbaniloyloxy) carbanilate	360	240
desmedipham	3-phenylcarbamoyloxy-phenylcarbamate	360	240
ethofumesate	(±)-2ethoxy-2,3-dihydro-3,3-dimethylbenzofuran-5-yl methanesulfonate	360	240

Sampling of soil and roots of sugar beet was carried out on the day of sugar beat lifting. 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 a soil depth of 0-20 cm.

Samples from each plot were well mixed and stored in polyethylene bags at minus 18 °C until sample extraction. Soil moisture content was determined for each soil sample. The samples were dried at 105 °C for 24 h.

Determination of residues

Phenmedipham, desmedipham and ethofumesate were extracted twice from

30 g soil and root of sugar beet samples using a mixture of 150 mL methanol and methyl chloride (1:1 V/V). The samples were mixed and shaken at 200 rev. min^{-1} for 20 min on a horizontal shaker and filtered under reduced pressure.

The extracts were cleaned by solid-phase extraction using preconditioned SPE cartridges with 1g of florisil (J.T. Baker). Elution of the samples was carried out using 10% solution of ethyl acetate in methylene chloride (V/V). The extracts were evaporated to dryness and the dry residue was dissolved in 4 mL of mixture: 5% of isopropanol and 95% of heksane (V/V).

All samples were analysed 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 DuPont ZORBAX SIL (4.6 x 25 mm) column and 5% of isopropanol + 95% of heksane (V/V) as mobile phase at a flow rate of 0.4 mL min^{-1}. The injection volume was 20 μL and detection was performed at 240 nm. All chemical reagents used in analytical procedure (delivered by Merck Corp.) were class: for synthesis (purity ≥99.5% – extraction) and for liquid chromatography LiChrosolv (purity ≥ 99.8% – dilution and mobile phase).

The recoveries of the active substances were 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, mixed well and extracted as described above. The average recoveries and quantification limits of the method for all concentrations are given in Table 3.

Table 3. Recoveries and quantification limits of the analytical method

Tested substance	Average recoveries [%]		Limit of detection* [mg kg^{-1}]	
	soil	roots	soil	roots
phenmedipham	95	89	0.0001	0.0001
desmedipham	90	84	0.0001	0.0001
ethofumesate	86	76	0.0005	0.0005

* for 30 g of sample

Analytical procedure described above was performed at the Institute in Laboratory of Residue Research [10]. All results of residue concentration were calculated to dry weight of soil.

Results of residue data from field trials were calculated using the statistical program Statgraphics Plus for Windows, version 1.41 PL.

RESULTS

At lifting time, almost all samples of soil and about 86% of sugar beet samples contained detectable residues of herbicide active substances. The level of residues depended on the kind and dosage of substance, addition of adjuvant and weather condition in individual vegetation seasons. Results obtained from all experiments are shown in Tables 4 and 5.

Table 4. Residues of phenmedipham, desmedipham and ethofumesate in soil

Treat-ment	Residues* [mg kg^{-1}]								
	phenmedipham			desmedipham			ethofumesate		
	2003	2004	2005	2003	2004	2005	2003	2004	2005
FD	0.0390	0.0105	0.0179	0.0306	0.0167	0.0199	0.0218	0.0073	0.0095
RD	0.0263	0.0070	0.0093	0.0193	0.0068	0.0104	0.0133	0.0022	0.0042
RD + A1	0.0310	0.0084	0.0132	0.0238	0.0107	0.0122	0.0172	0.0036	0.0058
RD + A2	0.0326	0.0077	0.0139	0.0226	0.0098	0.0146	0.0164	0.0050	0.0046
RD + A3	0.0274	0.0086	0.0152	0.0249	0.0074	0.0145	0.0159	0.0028	0.0073
$LSD_{0.05}$	0.00492	0.00175	0.00337	0.00434	0.00334	0.00363	0.00289	0.00249	0.00246

* average residues for 4 replications, FD – full (recommended) dose, RD – reduced dose
A1 – adjuvant Olemix 84 EC, A2 – adjuvant Actirob 842 EC, A3 – adjuvant Break Thru S-240
LSD – least significant difference

Table 5. Residues of phenmedipham, desmedipham and ethofumesate in sugar beet roots

Treat-ment	Residues* [mg kg^{-1}]								
	phenmedipham			desmedipham			ethofumesate		
	2003	2004	2005	2003	2004	2005	2003	2004	2005
FD	0.0065	0.0015	0.0056	0.0060	0.0012	0.0033	0.0026	0.0008	0.0010
RD	0.0047	0.0006	0.0022	0.0021	0.0005	0.0015	0.0013	ND	0.0005
RD + A1	0.0058	0.0010	0.0046	0.0054	0.0007	0.0019	0.0011	ND	ND
RD + A2	0.0047	0.0007	0.0036	0.0030	ND	0.0016	ND	0.0005	ND
RD + A3	0.0062	0.0009	0.0024	0.0038	0.0008	0.0024	0.0014	0.0006	0.0006
$LSD_{0.05}$	0.00136	0.00050	0.00138	0.00147	0.00022	0.00075	0.00112	-	-

* Explanation as for Tab. 4, ND – residues not detected

DISCUSSION

The highest concentration of herbicide active substances was determined in samples from plots, where herbicide was applied at full (recommended) dose.

Reduction of herbicide dose caused a decrease of residues. The addition of adjuvants caused an increase of the herbicide active substance residue in soil and roots of sugar beet samples in comparison with the plots, in which reduced dose of herbicides were used without adjuvants. The increase of the herbicide active substance residue was statistically significant for 52% of soil samples and 33% of sugar beet root samples. The levels of herbicide active substance residues determined in samples with adjuvants were lower than in plots with the full recommended dose.

Other authors obtained similar results with adjuvants of: trifluralin [11, 12], atrazine [13] and phenmedipham [14].

Influence of adjuvants on herbicide residues was observed in experiments conducted in green house condition. Swarcewicz [11] and Swarcewicz et al. [12] described experiments in which influence of adjuvants on trifluralin degradation were tested. Fifty days after application residues of trifluralin amounted 38% of initial dose and in treatments with adjuvants residues ranged from 42 to 49% of initial dose. Similar experiment [15] also proved that the addition of adjuvants slowed down the degradation and increased the level of phenmedipham residue in soil. DT50 value (dissipation time for 50% of the initial residue to be lost) for mixture phenmedipham + adjuvants was about 10 days higher in comparison with DT50 for phenmedipham applied alone.

In our experiment residues of Betanal active substances determined in roots of sugar beet did not exceed maximum residue limit (0.1 mg kg^{-1}). Application of herbicides with adjuvant allowed to reduce the herbicide dose (without lost of weed control efficacy) and therefore limited the risk for agricultural environment.

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