

HERBICIDE RESIDUES' CHANGES IN WHEAT SAMPLES IN LATE WEED CONTROL

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Since the change of the Hungarian agriculture the increased weed infection causes great losses in wheat. It is necessary to apply herbicides on the weedy field as harvest approaches to make the harvest easier and avoid losses. In our small plot trials at Nagygyombos, between 1996 and 2002 the applicability of fluroxypyr, bromoxynil, dicamba, tribenuron-methyl and MCPA in late weed control was examined in four wheat varieties. We found that the late application against weeds did not have a total eliminating effect, however reduced the number of weeds, restricted their development and the reproductive organs below and above ground dried. Weed seed infection was slowed down and the dried stems made harvesting easier. In the last three years, we found that fluroxypyr (Starane) and tribenuron-methyl (Granstar) impeded a little the maturing and water extraction in the milk maturation stage of wheat, but this difference was not seen in full maturation. Examinations showed that after late weed control, all of above-mentioned chemicals except bromoxynil (Pardner) was discharged at the time of the harvest and were under the maximum residue tolerance limit. So the experimentally involved herbicides can be used for late weed control – in accordance with international experiences.

Keywords: wheat, late weed control, herbicide residue, chemical breakdown

The Hungarian agriculture in general and the wheat production in particular was influenced unfavourably by the economic changes since 1990. The technological development and disciplined management characteristics of our crop production were slowed down. Therefore, great weed problems arose that were thought to be controlled during the last 20 years. On the fallowed, neglected fields weed infection is as high as it was in the fifties (NÉMETH, 2001). According to PINKE and co-workers (1997), some of the reasons of increased weed infection are the higher precipitation and the ineffective weed control practices. The less intensive tillage of small holdings contributes, in great part, to the advancement of perennial weeds (BENÉCSNÉ, 1998).

This situation requests the elaboration of new methods from research. Therefore, in our trial a less frequently employed, but well known in wheat technology, late weed control was used after fertilization (in the development stage Fekes-10.5.4.). Such weed control for the facilitation of harvest is not unknown in global agriculture and we have the appropriate chemicals. In Hungary the Roundup Bioaktive containing glyphosate is

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well known. Naturally, it cannot be expected from the treatment to eliminate weeds totally. The treatment dries plants more or less, inhibits or reduces seed production, and the wheat containing dried weeds can be harvested more easily.

GREER and PEEPER (2001) from the Oklahoma University have mentioned practical advises for weed control of wheat. They emphasized that herbicides may not be used in the stage of earing, but after it, during the grain filling Banvel (dicamba) and 2,4-D may be applied. The NEBRASKA EXTENTION SERVICE (2000) advises that 2,4-D should be used between tillering and shooting, but not after it. If the field is extremely weedy before the harvest and the grains already are hard, 2,4-D may be used against weeds without harming the wheat.

HAGER and SPRAGUE (2001) from the Agricultural and Environmental State University of Georgia have suggested that glyphosate-containing chemicals could be used at 30% or lower grain moisture content. JOHNSON and FISHEL (2000) have shown that herbicide active agents such as bromoxynil 2,4-D, dicamba, MCPA, tribenuron, bromoxynil+MCPA were used in late weed control in Missouri. The advises for application were the same as known already.

Chemicals applied by this method may be present on the surface and inside the plants used for nutrition. Each of these chemicals, which are present in the plant, may cause acute or potential danger to human health. Therefore, analytical tests for monitoring chemical residues in foods are extremely important. Since the residues are present in small content, only highly sensitive chromatographic methods can be used such as gas chromatography (GC), HPLC and the thin layer chromatography.

GRORUD and FORETTE (1983) have proposed the use of HPLC method for the determination of 2,4-D, dicamba and 2-(2-methyl-4-chlor-phenoxy) propionacid herbicides, and gas chromatography for the determination of bromoxynil-octanate. McDONALD and co-workers (1994) developed a HPLC method for the separation of fluroxypyr also used in our trial, with the help of which the breakdown mechanism of the chemical can be traced.

CESSNA and HUNTER (1993) analysed dicamba residues for two years in wheat in 420 and 140 g ha⁻¹ treatments. They found that the residues were decreasing rapidly after the treatments, and were below 0.1 mg kg⁻¹ after 5–6 weeks. 2,4-D could not be detected in the mature grain. Dicamba in the grain was not detected in the first year, but appeared in 0.065±0.014 mg kg⁻¹ concentration in the second.

1. Materials and methods

Trials were set in the Hatvan-Nagygyombos area on plots with 10 m² size in four randomized replications. Herbicide was applied with a commercial weed-sprayer in each plot, and the active agent/hectare was calculated for plots. Samples were taken randomly from the plots receiving treatment.

In the examined period between 1996 and 2002 pre-crops were in each case horticultural plants, which belong to weed-promoting cultures. The field was therefore similar to the neglected weed situation seen in Hungary and the technology of late weed control could also be modelled well.

In our trials four wheat cultivars were used: Mv-21, Fatima 2, Mv-Magdaléna and Alföld-90. Prior to weed control treatments, a weed survey was carried out (NÉMETH & SÁRFALVI, 1998). Weather can be described shortly by saying that precipitation was relatively favourable until 2000, but these were followed by drought. The plant protection chemicals used in the trial are shown in Table 1. Late weed control was carried out after fertilization – in the Fekes-10.5.4. development stage – at the dates shown in Table 2.

Table 1. Active agents, herbicides and allowed active agent residues in mature wheat (Nagygyombos, 1996–2002)

Active agent	Name and dose of the commercial product	Tolerance limit (mg kg ⁻¹) ^a
Fluroxypyr	Starane 250 EC, 0.8 l ha ⁻¹	0.1
Bromoxynil	Pardner, 1.5 l ha ⁻¹	0.02
Dicamba	Banvel 480 S, 0.2 l ha ⁻¹	0.1
Tribenuron-methyl	Granstar 75 DF, 25 g ha ⁻¹	0.05
MCPA	Triton 320 SL, 3 l ha ⁻¹	0.1

^a On the basis of SZABADI (2002)

Table 2. Dates of weed control treatments, sampling and harvest, Nagygyombos

Year	Late weed control treatments	Sampling 1	Sampling 2	Sampling 3 harvest
1996	30.05.	07.06.	26.06.	03.07.
1997	06.06.	03.06.	01.07.	08.07.
1998	30.05.	06.06.	24.06.	21.07.
2000	28.05.	04.06.	22.06.	21.07.
2001	06.06.	12.06.	30.06.	16.07.
2002	30.05.	07.06.	28.06.	11.07.

After carrying out the late weed survey, the water extraction of the plants was monitored (SALGÓ & GERGELY, 2003) and the breakdown and discharge of herbicides from wheat plants were analysed. Samples were taken three times. The first two were taken from the ears of green plants on days 7–8 and 18–21 after spraying (Table 2). Samples were stored deep-frozen until laboratory analysis. The third sample (3) was taken after harvest, from the air-dry grains. Samples were analysed by the Biochemical and Food Technology Department of the Budapest University of Technology and Economics.

The process of the evaluation of the samples was the following. Deep-frozen samples were thawed and the water and dry matter content of the wheat in that certain development period was determined. Water content of the samples was determined by drying at 105 °C in a drying-cabinet until equilibrium.

Extraction of herbicides from the wheat samples: wheat plants were cut into small pieces by a pair of scissors, 25 g of each was put into a 250 cm³ Erlenmeyer test-tube. Ten cm³ sulphuric acid diluted in water (1:1) and 100 cm³ acetone–petroleum ether (1:1) were added to the samples. The sample was further chopped with an Ultraturax, was mixed and filtered on a G4 glass filter. The solid residue was washed with 10 cm³ acetone–petroleum ether mixture. It was extracted again in the same way by 150 cm³ acetone–petroleum ether mixture, was treated for 10 min in an ultrasonic bath and filtered on the G4 glass filter, and the test-tube and the residue were washed with 20 cm³ acetone–petroleum ether mixture. The united extract was carried over to a 500 cm³ shaking funnel and 200 cm³ of water was added to it. The hexane upper phases and the heavier water–acetone phases were separated after mixing the sample. The lower phases were extracted 3 times; 50 cm³ of dichloro-methane and the dichloro-methane phases were mixed with the hexane phases. The united phases were evaporated in a Rotadest evaporator to the final volume of 20 cm³. Fifty cubic centimetre of benzene was added and evaporated to dryness and the rest was dissolved in 10 cm³ of acetone. Recovery checks were performed for three pesticides with fortified samples.

The samples of active agent fluroxypyr, bromoxynil and dicamba were analysed with a Fisons GC 8000 gas chromatograph. Parameters of gas chromatography were as follows:

Column: DB-1 HRGC column, product of J&W Scientific; Length: 30 m; ID: 0.32 mm; film: 1 µm methyl-silicon.

Mobil Phase: Nitrogen 32 cm s⁻¹; Pressure: 100 kPa; Split: 20.

Temperature: Thermostat: 260 °C; Injector: 280 °C; Detector: 300 °C.

Detector: Ni89 ECD 800; Pulse amp: 50 V; Pulse width: 1 µs; Make up: nitrogen 150 kPa. The sample quantity was 1 µl.

The samples of active agent tribenuron-methyl and MCPA were analysed by HPLC with a Waters apparatus using UV detection. The tendency of discharging active agents were determined and calculated by the function analysis of the Excel program.

2. Results and discussion

2.1. Water content

Water content was always around 62–71% each year. Wheat was at this time in the grain filling stage before milk ripening. At the time of the second sampling, grains were in the milk ripening stage and had 32–40% water content depending on the weather. The third sample was taken at 11–14% air-dry condition. These results would not have any special significance if an extraordinary effect had not been found in the samples taken in 2000. In the last three years, measurements showed that certain chemicals,

mainly fluroxypyr (Starane) and tribenuron-methyl (Granstar) could delay a little the maturation and water extraction of the wheat plants at this development stage. This difference was not seen by the time of ripening. Evidence of such effect of these herbicides was not found, therefore, further research would be necessary to answer this question.

2.2. Discharge of herbicides

In Tables 3 and 4 two results are demonstrated for each year and for each chemical concerning the discharge of the herbicides involved. The data of these tables show that in each year data of each variety have a high, but changing starting point, which decrease after about 25 days and have an extremely low value in the mature grain. These values were in most cases lower than the alimentative limit, and even if they were not below, they were just around it. This tendency was observed in case of each chemical with the exception for Pardner containing bromoxynil active agent. The limit value in case of this chemical is so low (0.02 mg kg^{-1}) that it was often above the limit in the find-products.

Table 3. Discharge of dicamba (Banvel) in the examined years (residual values, mg kg^{-1}), Nagyombos

Sampling time	Years											
	1996		1997		1998		2000		2001		2002	
	Cultivars											
	Mv-21	Fatima	Mv-21	Fatima	Mv-21	Fatima	Mv- Magdaléna	Alföld	Mv- Magdaléna	Alföld	Mv- Magdaléna	Alföld
1st	38	29.8	21.29	3.06	7.76	4.81	0.038	0.085	2.07	2.12	9.82	5.94
2nd	1.5	2.0	0.34	0.32	3.95	2.17	0.005	0.002	0.06	0.012	0.64	0.38
3rd	0.41	0.35	0.05	0.042	0.089	0.45	0	0	0.002	0.007	0.004	0.002

Sampling times in Table 2

Table 4. Discharge of MCPA (Triton) in the examined years (residual values, mg kg^{-1}), Nagyombos

Sampling time	Years					
	2000		2001		2002	
	Cultivars					
	Mv-Magdaléna	Alföld	Mv-Magdaléna	Alföld	Mv-Magdaléna	Alföld
1st	0.14	0.53	1.12	1.65	3.30	3.687
2nd	0.009	0.0035	1.0	1.0	0.214	0.239
3rd	0.003	0.0015	0.0015	0.008	0.001	0.001

Sampling times in Table 2

There are two reasons for the great and mainly initial quantitative deviations. Firstly that in spite of such sensitive and accurate analyses, the standard deviation is significant. Secondly, if immediately or soon after the spraying smaller rain or greater dew appeared, the concentration decreased drastically. By the time of the second sample

the decrease of concentration was significant. The reason for the decrease was the chemical breakdown of the chemicals and even though the precipitation during these 20–25 days was in most cases not too high, accelerated the elimination of the chemical. During this time, the herbicide could take its effect on the weeds.

By the time of the third sampling, the chemical residue content in the mature grains was lower than the alimentative limit, or decreased below the detection limit. During these years, comparing the cultivars, no consequent tendencies could be determined, meaning that no cultivar effect or cultivar sensibility was registered. It could also be seen that if in the given year the initial concentration of the spraying material was higher, it was more or less equal for each type of chemical.

Limit values measured for chemicals are summarized and averaged in Table 5. The summarization shows that all chemicals broke down to such an extent that they were below the alimentative limit values – with the exception of bromoxynil (Pardner), or in the case of dicamba were just around that. There was a similar case with the highly effective tribenuron-methyl (Granstar). Therefore, the examined chemicals can be used for safe late weed control, in accordance with international experiences, with the exception of Pardner, which does not break down below the tolerance limit value during 45 days. This and its lower effectiveness may be the reasons why international consultative literature does not propose bromoxynil for late weed control.

Table 5. Summarized discharge values in the examined chemicals (residual values, mg kg⁻¹), Nagygyombos

Sampling time	Herbicides				
	Fluroxypir (Starane)	Bromoxynil (Pardner)	Dicamba (Banvel)	Tribenuron-methyl (Granstar)	MCPA (Triton)
1st	10.42	15.54	10.39	2.34	1.738
2nd	2.59	1.85	0.94	0.099	0.411
3rd	0.076	0.104	0.117	0.0027	0.003
Limit value	0.1	0.02	0.1	0.05	0.1

Sampling times in Table 2

Table 6. Mathematical expression of the tendencies of discharge of chemicals

Herbicide	Equation
Fluroxypyr – Starane	$y=2.658x^2-15.804x+23.566$
Dicamba – Banvel	$y=4.3135x^2-22.391x+28.467$
Tribenuron-methyl – Granstar	$y=1.0724x^2-5.458x+6.7257$
MCPA – Triton	$y=0.4595x^2-2.7055x+3.984$

The discharging tendency of the active agents follows an exponential decrease that can be described as in Table 6. The $y=x^2$ value shows how high the starting point of the status is, and how steeply it decreases. The highest value was measured for dicamba active agent, where after the high starting value, a fast decrease could be detected. This correlation may be generalized, since the tendency of decrease can be calculated by such a mathematical method, and from the speed, and the final value, the effectiveness can also be deduced.

3. Conclusion

Active agents of herbicides fluroxypyr, bromoxynil, dicamba, tribenuron-methyl and MCPA were examined in late weed control with several wheat varieties. The spreading of these herbicides was at the time of the ear emergence. After treatment, wheat samples were taken on the 7th, 24th day and from the harvested grains. The residues of active agents of herbicides were extracted from the wheat and grain samples, and the discharge of active agents of herbicides was measured by gas chromatography and HPLC analyses. It was proved that late application of the examined herbicides – if needed – is possible. Except for bromoxynil (Pardner), the tested herbicides were safely eliminated from the grains before the harvesting time.

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