

Effects of interaction and effectiveness of weed control when using tank mixtures of herbicides in maize crops

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Many countries are now facing the problem of increase in resistant biotypes of weeds. The spread of herbicide-resistant weeds across agrophytocenoses poses a threat of decrease in the effectiveness of use of herbicides in agricultural fields. In order to develop anti-resistant compositions of herbicides for protection of maize (*Zea mays* L.) crops, we studied effects of interaction and efficiency of weed control in greenhouse and field experiments. We studied the possibility of combined use of 4-hydroxyphenyl pyruvate dioxygenase-inhibiting herbicide tolypyralate and inhibitor of transport of electrons in photosystem 2 of chloroplasts – terbuthylazine – and acetolactate synthase-inhibiting rimsulfuron. In greenhouse experiments on model objects, we found that interaction in the mixtures of tolypyralate with rimsulfuron was antagonistic, but the antagonism may be overcome by increasing the rate of applied rimsulfuron. At joint use of tolypyralate and terbuthylazine, a synergistic increase in phytotoxic effect was observed, caused by increase in the effectiveness of the blocking electron-transport chain and increase in intensity of formation of reactive oxygen species. According to the results of the field experiments, we drew the conclusion that the efficacy of using the mixture of tolypyralate and rimsulfuron depends on the species composition of weeds. In the presence of rimsulfuron-resistant weeds, interaction with tolypyralate becomes antagonistic even in the conditions of increased rate of application of rimsulfuron, and thus the effectiveness of the protection significantly decreases. At the same time, after applying tank mixture of tolypyralate with terbuthylazine, the synergistic character of the interaction was maintained toward a broad range of species of grass and dicotyledonous weeds, providing high efficiency of maize crop protection. The herbicide compositions that were analyzed and are presented in the article allow one to decrease the possibility of emergence of resistant biotypes of weeds, and also to effectively control the already existing resistant biotypes.

Keywords: resistance of weeds; tolypyralate; terbuthylazine; rimsulfuron; synergism and antagonism in herbicide combinations.

Introduction

Maize is very sensitive to negative impact of weeds. Therefore, a necessary condition for obtaining high yields of maize is effective protection of crops from weeds. To protect maize, a number of highly-efficient herbicides are available, particularly of the class of inhibitors of acetolactate synthase (ALS), which, in addition to the high effectiveness of weed control, are also noted for their environmental safety. However, broad-scale use of ALS-inhibiting herbicides in maize and other crops resulted in emergence of weeds that are resistant to those herbicides (www.weedscience.org/Pages/Herbicide.aspx#). In general, the emergence and spread of herbicide-resistant biotypes is considered to be the main problem of the current chemical method of weed management (Powles & Yu, 2010; Vencill et al., 2012; Kraehmer et al., 2014). Uncertainty about how to solve this problem calls into question the future prospects for large-scale use of herbicides (Shaw, 2016; Barrett et al., 2017; Harker et al., 2017; Kozak et al., 2020; Tkalich et al., 2021; Tsyliuryk et al., 2021).

Currently, it is considered that the only way to prevent the emergence of resistance is alternating herbicides with various mechanisms of phytotoxicity and complex application of herbicides for protection of certain cultivated plants during crop rotation (Diggle et al., 2003; Beckie, 2006; Norsworthy et al., 2012). Currently, the search for herbicides with new mechanisms of phytotoxicity is unsuccessful and financially expensive, and therefore one of the possible solutions to this problem may be creating herbicide complexes of already existing substances (Rüegg et al., 2007; Duke, 2012; Duke et al., 2019). Herbicide complexes are broadly used to

increase the efficiency of weed control. However, a large proportion of the complex herbicide substances or tank mixtures of herbicides which have so far been broadly utilized for protection of maize has proved less effective for resistance prevention. First of all, in many cases, active substances with one action mechanism are being combined, particularly MaisTer Power preparation, the active substances of which are three inhibitors of ALS. Combining active substances that share a common action site is known to be highly likely to interact synergically (Morderer & Merezhynsky, 2009), whereas to combat the resistance, herbicides with various phytotoxicity mechanisms need to be used. Another disadvantage of existing herbicide compositions is the fact that action ranges of their components match only partly and most weed species become subjected only to the action of one of the constituents. In particular, combinations of ALS-inhibiting herbicides and synthetic auxins, namely dicamba (Task and Task Extra preparations), act exclusively as ALS inhibitors against grass weeds, while joint action of both the constituents occurs only toward some species of dicotyledonous weeds. At the same time, to prevent the resistance, compositions the constituents of which vary by mechanisms of phytotoxic action are needed, but the ranges of their action need to significantly match (Norsworthy et al., 2012). Furthermore, a necessary requirement for high efficacy of weed control is obviously the additivity or synergistic pattern of interaction of constituents of those compositions.

Herbicides that inhibit 4-hydroxyphenyl pyruvate dioxygenase are a recently opened class of herbicides, belonging to the 27th class of herbicides (Sherwani et al., 2015). Therefore, the resistance to this class of herbicides has not yet become as widespread as resistance to ALS-

inhibitors (Heap, 2021). The analysis of studies of interaction of inhibitors of hydroxyphenyl pyruvate dioxygenase with herbicides of other classes may lead to a conclusion that their best partners at the moment are ALS-inhibitors (Duus et al., 2018) and herbicides that inhibit electron transport in the photosystem of 2 chloroplasts (PS II) (Armel et al., 2005; Walsh et al., 2012). Especially promising for developing such mixtures may be a new herbicide of the class of inhibitors of hydroxyphenyl pyruvate dioxygenase – tolpyralate (Kikugawa et al., 2015; Tonks et al., 2015; Metzger et al., 2018). When combining herbicides, phytotoxic action of the mixture's constituents may change, and therefore it is important to understand the mechanisms of interaction. The ultimate death of plant cells during pathogenesis, induced by herbicides with various phytotoxicity mechanisms, is known to occur through the mechanism of programmed cell death (Morderer et al., 2013). At the same time, the action of herbicides, the phytotoxicity of which is caused by disorganization of photosynthesis, is mediated by formation of reactive oxygen species (Hess, 2000), which likely act as inductors of programmed cell death (Chen & Dickman, 2004; Graham, 2005).

Thus, there are two possibilities of complex use of herbicide that inhibits hydroxyphenyl pyruvate dioxygenase – tolpyralate – for protection of maize fields and prevention of development of resistance of weeds to herbicides: application in mixtures with herbicides that inhibit ALS or with inhibitors of electron transport. Comparison of advantages and disadvantages of those two ways was the objective of this study.

Materials and methods

The effects of interaction of herbicides were determined in greenhouse experiments, while the effectiveness of weed control and selectivity to maize were determined in field experiments. For complex application with tolpyralate, we used ALS-inhibitor, rimsulfuron, and inhibitor of PS II electrons transport, terbuthylazine, allowed in Ukraine for use in maize crops. We used the following herbicides: Ashitaka MD (tolpyralate, 100 g/L), Promatrix KS (terbuthylazine, 500 g/L), Titus (rimsulfuron, 250 g/kg). Herbicides tolpyralate and terbuthylazine were used in the rates, respectively 30g/ha and 750 g/ha. Rimsulfuron was applied in the recommended rate of 10 g/ha in the preliminary greenhouse experiment, and in double rate of 20 g/ha in the subsequent greenhouse and field experiments. To the operating solutions of tolpyralate and rimsulfuron, we added Mero adjuvant in the rate of 1.5 L/ha (0.75%). Variants of the experiment: 1 – control; 2 – Tolpyralate (30 g/ha) + Mero (1.5 L/ha); 3 – Rimsulfuron (10 g/ha; 20 g/ha) + Mero (1.5 L/ha); 4 – Tolpyralate (30 g/ha) + rimsulfuron (10; 20 g/ha) + Mero (1.5 L/ha); 5 – Tolpyralate (30 g/ha) + terbuthylazine (750 g/ha) + Mero (1.5 L/ha); 6 – Terbuthylazine (750 g/ha).

In the greenhouse experiments, as models of annual dicotyledonous weeds, we used plants of *Raphanus sativum* d. var. *oleifera* Metrg. The plants were grown in plastic pots (4 pots for each variant) of the area of 0.015 m², which contained 1.3 kg of soil (mixture of soil with sand in the proportion of 3:1) on a vegetative plot and in a mini-phytothrone under luminescent lamps (photoperiod: day-night – 16/8). The plants were sprayed with herbicide solutions in the stage of 2–3 true leaves. The rate of application of herbicides was calculated for the area of the pot.

In greenhouse experiments, the dynamics of development of phytotoxic action of herbicides was determined according to the effect on accumulation of photosynthetic pigments in leaves. The content of photosynthetic pigments was determined using spectrophotometric method by extracting a weighed amount of plant material into dimethylsulfoxide on a heated bath in 67 °C for 3 h (Welburn, 1994) and calculated per unit of dry matter.

In order to determine possible mechanisms of interaction, we also studied the effect of herbicides on induction of fluorescence and formation of reactive oxygen species, namely superoxide anion radical. Fluorescence induction allows one to evaluate the condition of the electron-transport chain of chloroplasts and therefore is broadly used to determine the harm the herbicides cause to plants (Dayan & Zaccaro, 2012; Weber et al., 2017). The results of determining Fv/Fm parameter characterize the highest quantum yield of photosynthesis. We measured fluorescence induction using Junior-Pam fluorometer (WALZ, Germany) and determined

maximum quantum yield of photosynthesis according to the ratio of parameters of fluorescence variability (Fv) to maximum (Fm), which we evaluated after the leaves had adapted to the dark after 20 minutes. Fluorescence variability (Fv) was determined according to the difference between maximum and minimum levels of fluorescence (Fm–Fo) (Maxwell & Johnson, 2000).

Concentration of superoxide anion radical was determined according to ability of homogenates of the tissues to reduce nitro blue tetrazolium. For this purpose, a weighed amount of plant material was homogenized in cooled mortars with 5 mL of 0.1 M of phosphate buffer (pH = 7.6), containing 1 mM of inhibitor of superoxide dismutase – sodium diethyldithiocarbamate and centrifuged at 7,000 rpm for 10 min. To 3 mL of supernatant, we added 1 mL of 0.05% nitro blue tetrazolium and incubated for 30 min in the dark in room temperature. Optical density was determined at $\lambda = 530$ nm, and the results were expressed in relative units. Measurement of physiological characteristics of phytotoxic action was repeated twelve times. Inhibitory action was expressed in percents and calculated according to the values of measured parameters in the experimental and control variants (Shorning et al., 2000).

Field experiments were performed in 2020–2021 in the fields of the experimental farm of the Institute of Plant Physiology and Genetics of National Academy of Sciences of Ukraine, Hlevaha village of the Fastiv district of Kyiv region (50°16' N, 30°18' E). The research farm is at the border of the Polissia and the Forest-Steppe zone. The climate is moderate, the annual amount of precipitations ranges 520 to 645 mm. Soil is sod-podzolized, loamy according to mechanical composition, the content of humus is 1.6%, pH – 5.6. The experiments were carried out in the crops of maize hybrids PR-39B76 (2020) and Vulkan M (2021).

The maize crops were treated in the stage of 5 leaves. The herbicides were sprayed using backpack herbicide bar sprayer with compressed air, 4 atm pressure, bar length – 3 m, number of nozzles – 6. The distance to target object was 50 cm, moving speed – 5 km/hour, expenditures of operating liquid – 300 L/ha. The area of the studied plot was 15 m² (3 x 5 m), the repetition was four times, the plots were allocated randomly. Each experiment included the control variant (with no herbicides).

The monitoring of weeds was carried out prior to spraying pesticides, after 15 and 30 days of the treatment and before the harvest. Effectiveness of action of herbicides was determined for each species of weed separately according to decrease in their number in the treated plots, compared with the control (Ivashchenko & Merezhytsky, 2001), taking into account visual assessment of the degree of inhibition of plants treated with herbicides, compared with the condition of those plants in the control (weight and linear sizes, chlorosis of leaves, etc). The inhibition level – according to the visual assessment – was expressed as a percentage: 0% – no signs of action of herbicides, 100% – complete death of weeds of this species. Effectiveness of the weed control was calculated according to inhibitory action of herbicides and their mixtures as percentages compared with the control. The effect of interaction of herbicides in the mixture was determined using the Colby (1967) method by comparing actual and expected effects of mixture of herbicides. The expected effect of herbicides was calculated taking into account the value of inhibitory action (effectiveness of weed control) of all components separately and in mixture.

Selectivity of herbicides to the cultivated plant was assessed according to the biometric measurements and phenological monitoring. The effect of herbicides was evaluated 7 days after the treatment of fields with herbicides and during every weed count, as well as by determining the effect of herbicides on maize grain yield.

The comparisons were carried out using the Tukey test with Bonferroni correction. The differences between the data were considered significant at $P < 0.05$. The results are presented as mean and standard errors ($\bar{x} \pm SE$).

Results

At the first stage, in the greenhouse experiment, we checked the pattern of interaction of tolpyralate and rimsulfuron, the latter being applied in the recommended rate of 10 g/ha. The dynamics of development of phytotoxic action, studied under the influence of herbicides on accumulation of photosynthetic pigments (Fig. 1), revealed that interaction of rimsulfu-

ron in the recommended rate of 10 g/ha with tolpyralate had signs of antagonism. In the variant with application of the mixture of tolpyralate and rimsulfuron, the inhibitory action on the accumulation of total chlorophyll (Fig. 1a) and carotenoids (Fig. 1b) significantly exceeded the action of rimsulfuron alone on third and sixth days after the treatment. The inhibitory action of rimsulfuron alone toward the accumulation of pigments was insignificant on the third and sixth days, but rapidly increased on the ninth day. At the same time, under the influence of the mixture of rimsulfuron and tolpyralate, no signs of increase in the inhibitory action on the ninth day after the treatment were seen. Excess of inhibitory action during the use of rimsulfuron alone compared with the action of mixture of rimsulfuron and tolpyralate is a clear sign of antagonistic interaction.

Dispersion analysis of the results of studying the effects of herbicides on the accumulation of photosynthetic pigments in leaves of *R. sativum* d. var. *oleifera* (Table 1) revealed a significant decrease in the content of total

chlorophylls on day five, compared with the control, in all variants where herbicides had been used. At the same time, the lowest effect on the content of chlorophylls was produced by the action of tolpyralate alone. On the eighth day, significant increase in the inhibitory effect on the accumulation of chlorophyll – compared with the fifth day – was seen in the variant with the use of tolpyralate alone and its mixtures with rimsulfuron and terbuthylazine. At the same time, we found no significant difference between the concentrations of chlorophylls in the variants where tolpyralate, rimsulfuron and terbuthylazine had been used separately. The lowest content of chlorophyll, and therefore highest inhibitory effect on its accumulation was seen in all variants with use of the mixture of tolpyralate and terbuthylazine, which significantly exceeded the actions of tolpyralate, rimsulfuron and terbuthylazine alone. The effect of the mixture of tolpyralate and rimsulfuron was lower than that of the mixture of tolpyralate and terbuthylazine.

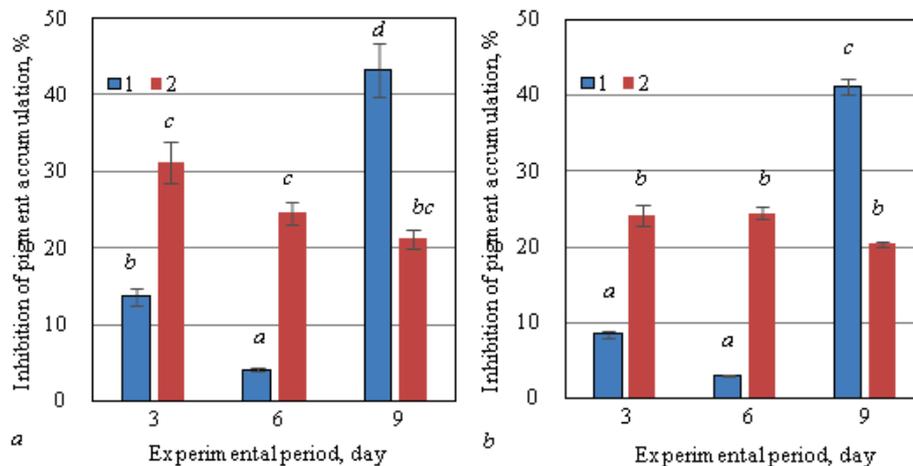


Fig. 1. Inhibitory effect of rimsulfuron herbicide (1) and its mixture with tolpyralate (2) on the accumulation of total chlorophyll and carotenoids in leaves of *R. sativum* d. var. *oleifera*: a – total chlorophylls; b – carotenoids; compared using Tukey test; n = 12; x ± SE

Table 1

Content of total chlorophyll (a + b) and carotenoids (mg/g of dry matter) in leaves of *R. sativum* d. var. *oleifera* on the 5th and 8th days after spraying with the herbicides (x ± SE; n = 12)

Variant	Total chlorophyll a+b		Carotenoids	
	5 th day	8 th day	5 th day	8 th day
Control	3.41 ± 0.13 ^a	3.29 ± 0.19 ^a	0.671 ± 0.010 ^a	0.641 ± 0.017 ^a
Tolpyralate (30 g/ha) + Mero (1.5 L/ha)	2.51 ± 0.05 ^b	1.97 ± 0.10 ^{bc}	0.540 ± 0.042 ^b	0.415 ± 0.022 ^c
Rimsulfuron (20 g/ha) + Mero (1.5 L/ha)	1.84 ± 0.15 ^c	1.67 ± 0.15 ^c	0.388 ± 0.010 ^c	0.362 ± 0.014 ^c
Tolpyralate (30 g/ha) + rimsulfuron (20 g/ha) + Mero (1.5 L/ha)	2.04 ± 0.13 ^{bc}	1.22 ± 0.16 ^{cd}	0.401 ± 0.010 ^c	0.314 ± 0.008 ^c
Tolpyralate (30 g/ha) + terbuthylazine (750 g/ha) + Mero (1.5 L/ha)	1.81 ± 0.08 ^c	0.89 ± 0.05 ^d	0.484 ± 0.023 ^{bc}	0.199 ± 0.007 ^d
Terbuthylazine (750 g/ha)	1.93 ± 0.13 ^{bc}	1.78 ± 0.01 ^c	0.438 ± 0.029 ^{bc}	0.377 ± 0.030 ^c

Note: different letters indicate selections that significantly differ from each other at P < 0.05, compared using the Tukey test with Bonferroni correction; the comparisons were made within the columns.

Changes in the concentration of carotenoids which occurred during the action of herbicides did not differ radically, though they had some quantitative differences, compared with the content of chlorophylls. On day five, the concentration of carotenoids – compared with the control – decreased in all the variants, and the decrease in the variant with tolpyralate alone was lower than in the variants with rimsulfuron alone and in the mixture with tolpyralate. On day eight, the inhibitory effect on accumulation of carotenoids – compared with day fifth – significantly increased in the variants with use of tolpyralate alone and its mixture with terbuthylazine. At the same time, the inhibitory effect on accumulation of carotenoids in the variants with use of the mixture of tolpyralate and terbuthylazine was the highest, because the concentrations of carotenoids in the variant with the use of this mixture were significantly different from all the variants with the use of herbicides.

The data in Figure 2 show that between actual and expected inhibitory effects on accumulation of total chlorophylls and carotenoids, no significant difference was seen after using both types of mixtures. Based on the obtained data, we can confidently state only the absence of antagonism during the application of the mixture of tolpyralate and terbuthylazine, because we can see that utilization of this mixture results in a clear tenden-

cy toward excess of the actual inhibitory action over the expected one. The issue of overcoming the antagonism in the mixture of tolpyralate and rimsulfuron by increasing the rate of rimsulfuron remains unsolved, because during the action of the mixture, the expected inhibitory effect tended to exceed the actual one.

Measurement of fluorescence induction five hours after the treatment of plants with tolpyralate, rimsulfuron and the mixture of tolpyralate with rimsulfuron revealed no significant differences in the values of Fv/Fm parameter from the control (Table 2). Under the action of terbuthylazine, we saw a tendency toward decrease in Fv/Fm value, i.e. signs of blockade of electron-transport chain. At the same time, after the use of the mixture of tolpyralate and terbuthylazine, Fv/Fm parameter decreased by 66% compared with the control. Drastic decrease in the highest quantum yield of photosynthesis after the action of the mixture is evidence of synergistic interaction, and demonstrates that one of the factors determining synergistic interaction between tolpyralate and terbuthylazine is increase in efficacy of blocking electron transport in chloroplasts. This result may be considered as totally expected, since blocking electron transport by terbuthylazine and other herbicides with such a phototoxic action occurs because of competition between those

herbicides and plastoquinone for binding site with D1 reaction center protein of PS 2 in chloroplasts.

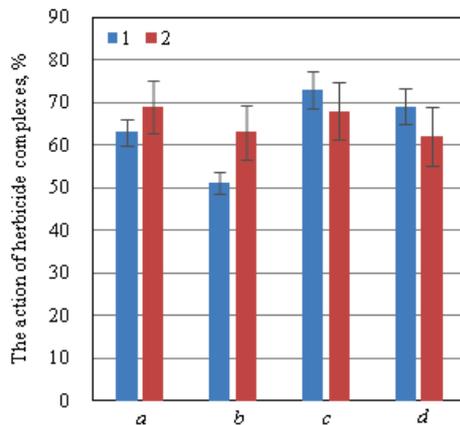


Fig. 2. Actual (1) and expected (2) inhibitory effects of the mixtures on day 8 after the treatment: tolpyralate and rimsulfuron (a, b) and terbuthylazine (c, d) on accumulation of chlorophylls (a, c) and carotenoids (b, d); the comparison was performed using the Tukey test, no significant difference between the actual and expected effects on day 8; n = 12; x ± SE

Table 2

Maximum quantum yield of photosynthesis (Fv/Fm) in leaves of *R. sativum* d. var. *oleifera* 5 h after the treatment with herbicides (x ± SE; n = 12)

Variant	Fv/Fm
Control	0.62 ± 0.02 ^a
Tolpyralate (30 g/ha) + Mero (1.5 L/ha)	0.60 ± 0.01 ^a
Rimsulfuron (20 g/ha) + Mero (1.5 L/ha)	0.63 ± 0.02 ^a
Tolpyralate (30 g/ha) + rimsulfuron (20 g/ha) + Mero (1.5 L/ha)	0.63 ± 0.04 ^a
Tolpyralate (30 g/ha) + terbuthylazine (750 g/ha) + Mero (1.5 L/ha)	0.21 ± 0.01 ^b
Terbuthylazine (750 g/ha)	0.58 ± 0.02 ^a

Note: different letters indicate selections that significantly differ one from another at P < 0.05, compared using the Tukey test with Bonferroni correction; Fv – variable fluorescence; Fm – maximal fluorescence.

Table 3

Concentration of superoxide anion radical (conventional units/g of dry matter) after the action of herbicides (x ± SE; n = 12)

Variant	5 h	48 h	120 h
Control	28.08 ± 0.64 ^a	32.71 ± 0.78 ^a	46.03 ± 1.10 ^b
Tolpyralate (30 g/ha) + Mero (1.5 L/ha)	25.37 ± 0.44 ^a	37.14 ± 0.67 ^{ab}	32.69 ± 0.42 ^a
Rimsulfuron (20 g/ha) + Mero (1.5 L/ha)	44.54 ± 0.22 ^b	41.81 ± 0.23 ^b	43.48 ± 0.70 ^b
Tolpyralate (30 g/ha) + rimsulfuron (20 g/ha) + Mero (1.5 L/ha)	49.04 ± 0.21 ^c	59.95 ± 1.09 ^d	55.50 ± 1.55 ^d
Tolpyralate (30 g/ha) + terbuthylazine (750 g/ha) + Mero (1.5 L/ha)	57.87 ± 0.21 ^d	67.22 ± 1.71 ^c	62.92 ± 0.70 ^c
Terbuthylazine (750 g/ha)	49.65 ± 0.20 ^c	54.68 ± 0.39 ^c	51.27 ± 0.16 ^c

Note: see Table 1.

Table 4

Weed infestation of maize crops in Kyiv Region, phase of their development prior to treatment with herbicides (tolpyralate, rimsulfuron, terbuthylazine and their mixtures) (x ± SE; n = 4)

Family	Species	Infestation, sp/m ²		Stage of development of weeds*		Height of plants, cm	
		2020	2021	2020	2021	2020	2021
Amaranthaceae	<i>Chenopodium album</i> L.	5.4 ± 0.21	5.1 ± 0.15	14–15	12–14	2.0 ± 1.0	1.5 ± 0.5
Asteraceae	<i>Cirsium arvense</i> (L.) Scop.	0	1.3 ± 0.02	0	30–32	0	15.0 ± 5.0
Asteraceae	<i>Matricaria inodora</i> L.	0.2 ± 0.002	1.1 ± 0.01	30–32	12–14	7.0 ± 1.0	6.5 ± 1.5
Asteraceae	<i>Lactuca serriola</i> L.	0.5 ± 0.009	0	32–34	0	22.5 ± 7.5	0
Asteraceae	<i>Ambrosia artemisiifolia</i> L.	0.5 ± 0.007	0	30–32	0	5.5 ± 0.5	0
Asteraceae	<i>Erigeron canadensis</i> L.	1.5 ± 0.03	0	10–12	0	1.0	0
Asteraceae	<i>Centaurea cyanus</i> L.	0	0.5 ± 0.003	0	13–15	0	9.0 ± 1.0
Brassicaceae	<i>Raphanus raphanistrum</i> L.	2.7 ± 0.05	5.4 ± 0.02	30–60	14–30	15.0 ± 5.0	9.0 ± 3.0
Geraniaceae	<i>Erodium cicutarium</i> (L.) L'Her.	0	1.2 ± 0.01	0	30	0	8.0
Poaceae	<i>Echinochloa crus-galli</i> (L.) Pal. Beauv.	40.1 ± 2.8	5.3 ± 0.21	13–15	13–14	7.5 ± 2.5	4.0 ± 1.0
Poaceae	<i>Setaria glauca</i> (L.) P. Beauv.	5.5 ± 0.22	10.5 ± 0.07	10–12	13–14	1.0	4.0 ± 1.0
Polygonaceae	<i>Polygonum aviculare</i> L.	5.3 ± 0.19	0	18–32	0	12.5 ± 2.5	0
Violaceae	<i>Viola arvensis</i> L.	3.6 ± 0.07	0	30–60	0	12.5 ± 7.5	0

Note: 0 – absence of this species that year; * – to determine development stages, we used globally recognized decimal systems introduced by companies Bayer, BASF, Syngenta, Horst (BBCH); the area of each experimental plot was 15 m².

The concentration of superoxide anion radical (O₂⁻) in leaves of *R. sativum* d. var. *oleifera* under the action of tolpyralate did not differ 5 and 48 hours after the treatment, and was even lower than in the control after 120 h (Table 3). Under the action of rimsulfuron, increase in the concentration of O₂⁻ was insignificant and brief, and only observed on the 5th and 48th h, and did not differ from the control on the 120th hour. Under the action of terbuthylazine, increase in O₂⁻ concentration was significant and observed throughout the monitoring. Under the combination use of tolpyralate and rimsulfuron, the concentration of O₂⁻ was significantly increasing compared with the effect of rimsulfuron alone, and did not differ in the 5th hour, and even exceeded the content of O₂⁻ in plants treated by terbuthylazine alone in the 48th and 120th hours. The highest content of O₂⁻, which significantly exceeded the level of O₂⁻ in plants treated with terbuthylazine alone throughout the study, was observed in the variant with the use of the mixture of tolpyralate and terbuthylazine. The results of determining the intensity of formation of O₂⁻ in leaves of *R. sativum* d. var. *oleifera* 5, 48 and 120 hours after herbicide treatment are presented in Table 3.

Increase in the rate of application of rimsulfuron when used in a mixture of tolpyralate changes the antagonistic interaction into additivity. When using a mixture of tolpyralate and terbuthylazine, the interaction was synergistic increase in phytotoxic action due to an increase in efficacy of blocking the transport of electrons and increase in the intensity of the formation of reactive oxygen species.

The results of the weed count, performed prior to the treatment with herbicides, are given in Table 4. In 2020, the field of maize was infested with 2 grass weed species, of which *E. crus-galli* dominated, and 7 species of dicotyledonous weeds, where the main threat to the sowings was posed by *Ch. album* and *P. aviculare*. During the further monitoring, the control variants experienced rapid increase in infestation with *S. glauca*, reaching up to 20 specimens/m². In 2021, infestation with grass weeds was much lower than in 2020. The main infesters among dicotyledonous weeds were *R. raphanistrum* and *Ch. album*, and among grasses – *S. glauca*.

In the conditions of 2020, use of tolpyralate alone provided almost complete control of plants of *E. crus-galli* (99.0 ± 1.0), with high efficiency, but 100% control was not achieved for *Ch. album* (96.8 ± 2.3) and *P. aviculare* (96.8 ± 2.7). Action of tolpyralate against plants of *S. glauca*, *E. canadensis* and *M. inodora* was average, the efficiency of controlling those species of weeds accounted respectively for 86.3%, 72.5% and 71.3%.

Efficiency of tolpyralate control of *A. artemisifolia* and *L. serriola* was below the average and equaled respectively 52.5% and 65.0%. Plants of *R. raphanistrum* (27.5 ± 5.4) and *V. arvensis* (0.0) were resistant to tolpyralate. In turn, terbuthylazine highly effectively controlled *Ch. album* (99.0 ± 1.0) and *M. inodora* (91.0 ± 4.5), averagely affected *V. arvensis* (87.0 ± 5.3) and *P. aviculare* (70.0 ± 4.9), poorly inhibited *R. raphanistrum* (55.0 ± 5.1), *L. serriola* (42.5 ± 5.3) and *A. artemisifolia* (37.5 ± 3.7) and had practically no effect on grass weeds and *E. canadensis* (0.0). Use of rimsulfuron alone highly effectively controlled *E. crus-galli* (94.3 ± 5.0), *R. raphanistrum* (92.0 ± 4.9), *M. inodora* (94.5 ± 2.7), *V. arvensis* (99.0 ± 1.0) and *E. canadensis* (96.8 ± 2.3). Rimsulfuron was averagely effective against *S. glauca* (78.8 ± 5.4), poor against *L. serriola* (65.0 ± 4.4) and had practically no effect on *Ch. album* (0.0), *P. aviculare* (0.0) and *A. artemisifolia* (0.0). Use of the mixture of tolpyralate and terbuthylazine produced practically 100% control of all weeds in maize fields. According to the ratio of actual and expected effects on *S. glauca* (98.0 ± 1.0/86.3 ± 5.3), *R. raphanistrum* (96.8 ± 2.0/67.4 ± 17.5), *L. serriola* (99.0 ± 1.5/79.9 ± 15.0), *A. artemisifolia* (99.0 ± 1.0/70.3 ± 8.4), *E. canadensis* (99.0 ± 1.0/72.5 ± 4.4), clear synergism was observed. Addition of tolpyralate to rimsulfuron increased the efficacy of controlling most weeds, compared with rimsulfuron and tolpyralate alone. At the same time, for *E. crus-galli*, *S. glauca*, *R. raphanistrum*, *L. serriola*, the actual efficacy of action of the mixture was not different from the expected one (99.0 ± 1.0/99.9 ± 6.0; 91.3 ± 1.3/97.1 ± 9.8; 96.8 ± 2.0/94.3 ± 15.3; 81.3 ± 3.0/87.8 ± 12.1). Against *A. artemisifolia*, the actual efficiency significantly exceeded the expected (98.4 ± 8.7/82.5 ± 1.0), while for *P. aviculare*, *V. arvensis* and *E. canadensis*, the expected action significantly exceeded the actual (96.8 ± 3.3/58.8 ± 6.0; 99.0 ± 2.0/62.5 ± 3.0; 99.1 ± 5.8/75.0 ± 2.3). Thus, the pattern of interaction of tolpyralate and rimsulfuron in the mixture depends on the species of weed. The action was additivity for the most of the species, even synergistic for one species, while antagonism occurred for some species. Decrease in the efficacy of the mixture of tolpyralate and terbuthylazine was seen against none of the species of weeds highly sensitive to one of the constituents, compared with the actions of one of the components. For species that were averagely sensitive to both of the components, no excess of the expected action over the actual was observed. By contrast, actual efficacy significantly exceeded the expected action toward *R. raphanistrum* (96.8 ± 2.0/67.4 ± 17.5), *A. artemisifolia* (99.0 ± 1.0/70.3 ± 8.4) and *E. canadensis* (99.0 ± 1.0/72.5 ± 4.4). This is evidence of synergistic interaction of hydroxyphenyl pyruvate dioxygenase-inhibiting tolpyralate and PS II electrons transport-inhibiting terbuthylazine.

In the conditions of 2021, tolpyralate highly effectively controlled grass weeds and *C. cyamus* (99.7 ± 1.4), acted against *R. raphanistrum* (92.5 ± 5.1) with higher effectiveness than in 2020, but had lower effect on *M. inodora* (30.0 ± 4.1). The effect of tolpyralate on perennial dicotyledonous weed *C. arvensis* (52.5 ± 3.2) was lower than average, while the annual dicotyledonous weed *E. cicutarium* (17.5 ± 9.7) was observed to be resistant to tolpyralate. Rimsulfuron highly effectively controlled grass weeds, *R. raphanistrum* (99.8 ± 1.2), *M. inodora* (99.8 ± 1.3), *E. cicutarium* (99.7 ± 1.1), and *C. cyamus* (99.0 ± 1.7). Rimsulfuron had close-to-average effects on *C. arvensis* (66.3 ± 8.5) and *Ch. album* (65.0 ± 10). We should note that action of rimsulfuron against *Ch. album* was significantly higher in 2021 than in 2020, which may have been conditioned by the earlier period of treatment, and therefore the earlier phase of the development of this weed. Terbuthylazine highly effectively controlled only *R. raphanistrum* (99.9 ± 1.7) and *Ch. album* (97.5 ± 2.7). The effects of terbuthylazine against other weeds were insignificant: *C. arvensis* (40.0 ± 6.1), *M. inodora* (40.0 ± 6.1), *C. cyamus* (48.3 ± 3.5), and practically absent against *S. glauca* (0). Use of the mixture of tolpyralate and rimsulfuron provided almost complete weed control, except for *C. arvensis* (actual 66.3 ± 7.8/expected 84.0 ± 11.5), which was controlled at the level of action of rimsulfuron alone. The expected effect of the mixture against this weed somewhat exceeded the actual, though as a result of high variability of the action of tolpyralate and rimsulfuron alone, this excess was not significant and may evidence antagonistic interaction. Against *M. inodora*, the expected effect exceeded the actual one (99.7 ± 10.6/87.5 ± 3.5). The actual effect was not different from the expected one against the following weeds: *E. crus-galli* (99.9 ± 1.4/99.9 ± 2.5), *S. glauca* (99.8 ±

1.4/99.7 ± 2.5), *R. raphanistrum* (9.9 ± 1.2/99.8 ± 5.2), *Ch. album* (99.8 ± 1.9/99.8 ± 10.7), *E. cicutarium* (99.8 ± 1.8/99.7 ± 10.9), *C. cyamus* (99.7 ± 1.5/99.8 ± 12.4). Use of the mixture of tolpyralate and terbuthylazine also produced practically 100% efficacy of weed control, except for *C. arvensis*, which was controlled at the level of 77.5 ± 5.8. At the same time, the actual effects of the mixture against *M. inodora* (97.5 ± 2.9/58.0 ± 15.3) and *E. cicutarium* (99.7 ± 1.5/38.1 ± 15.4) significantly exceeded the expected ones, evidencing synergic interaction. For weeds *E. crus-galli* (99.9 ± 1.5/99.3 ± 6.5), *S. glauca* (99.9 ± 1.3/99.3 ± 3.1), *R. raphanistrum* (99.8 ± 2.8/99.8 ± 5.2), *Ch. album* (99.8 ± 1.8/99.7 ± 5.2) and *C. cyamus* (99.7 ± 1.8/99.8 ± 3.2), the actual effects were not different from the expected ones. Further, the pattern of weed infestation of crops underwent of no significant changes. Phenological observations and biometric measurements revealed no negative effect of herbicides on the cultivated plant in any of the variants of the experiment.

In each of the years, maize in the control was strongly inhibited by weeds, whereas the utilization of herbicides resulted in obtaining significant increase in maize grain yield in both years of the monitoring (Table 5). Values of the yield correlated with the efficiency of controlling weeds that were the main infesters of the cultivated plants. The lowest gain in yield in 2020 was from the variants where rimsulfuron and terbuthylazine were used alone, and in 2021 – from the variants with using terbuthylazine alone. In 2020, the greatest values of yield, which were not different one from the other, were from the variants with using tolpyralate separately and the mixtures of tolpyralate and rimsulfuron and terbuthylazine, and in 2021 – from the variants with using tolpyralate and rimsulfuron alone and the mixtures of tolpyralate and rimsulfuron and terbuthylazine. At the same time, both years, highest values of yield was in the variants where the mixture of tolpyralate and terbuthylazine had been used.

Table 5

Grain yield of maize of hybrids PR-39B76 (2020) and Vulkan M (2021) after use of herbicides ($\bar{x} \pm SE$; $n = 4$)

Variant	Yield (T/ha)	
	2020	2021
Control	0.73 ± 0.01 ^a	1.81 ± 0.05 ^a
Tolpyralate (30 g/ha) + surfactant Mero (1.5 L/ha)	5.24 ± 0.29 ^e	6.71 ± 0.39 ^e
Rimsulfuron (20 g/ha) + surfactant Mero (1.5 L/ha)	3.30 ± 0.21 ^b	8.01 ± 0.43 ^{cd}
Tolpyralate (30 g/ha) + Rimsulfuron (20 g/ha) + surfactant Mero (1.5 L/ha)	5.93 ± 0.33 ^c	7.73 ± 0.41 ^{cd}
Tolpyralate (30 g/ha) + terbuthylazine (750 g/ha) + surfactant Mero (1.5 L/ha)	6.39 ± 0.22 ^c	8.33 ± 0.14 ^d
Terbuthylazine (750 g/ha)	3.04 ± 0.19 ^b	3.61 ± 0.07 ^b

Note: see Table 1.

Discussion

Herbicides of the class of inhibitors of hydroxyphenyl pyruvate dioxygenase are selective to maize and have broad spectrum of action and are potential partners for complex use of ALS-inhibiting herbicides in maize crops. However, the study revealed that interaction of inhibitors of hydroxyphenyl pyruvate dioxygenase and ALS was antagonistic (Schuster et al., 2008). Since this antagonism is not catastrophic and may be overcome by increasing the rate of application of ALS-inhibitors (Duus et al., 2018), use of mixtures of inhibitors of ALS and hydroxyphenyl pyruvate dioxygenase is possible. In particular, in Ukraine, Synhenta Company utilized registered preparation Eliumis, the active substances of which are ALS-inhibiting nicosulfuron and ALS-inhibiting mesotrione.

An alternative variant of complex application of herbicides in maize crops is application of hydroxyphenyl pyruvate dioxygenase-inhibiting herbicide mixed with electron transport-inhibiting herbicides. The advantage of this kind of mixture is the synergistic pattern of interaction of herbicides of those classes. In particular, synergic increase in phytotoxic effect was observed after using spray combination of hydroxyphenyl pyruvate dioxygenase-inhibiting mesotrione with various inhibitors of electron transport: atrazine (Armel et al., 2005; Walsh et al., 2012), atrazine and bentazon (Armel et al., 2008), metribuzin, atrazine and bromoxynil (Abendroth et al., 2006), bromoxynil and simazine (Willis et al., 2007). Synergistic increase in phytotoxic action in combination with electron trans-

port inhibitors was observed not only for mesotrione, but also hydroxyphenyl pyruvate dioxygenase-inhibiting topramezone and tembotrione. Importantly, combination with transport electron inhibitors caused no decrease in selectivity of hydroxyphenyl pyruvate dioxygenase inhibitors to sugar corn, which is more sensitive to those herbicides than common maize (Choe et al., 2014). Mixtures of hydroxyphenyl pyruvate dioxygenase-inhibiting mesotrione and isoxaflutole with electron transport-inhibiting metribuzin (O'Brien et al., 2018) were proposed to use to control biotypes of *Amaranthus tuberculatus* weeds that are cross-resistant to inhibitors of hydroxyphenyl pyruvate dioxygenase and atrazine. It was determined that the pattern of interaction depends on resistance of weeds: the interaction is synergistic for most sensitive biotypes, and additivity for more resistant (O'Brien et al., 2018). The necessity to increase the rate of application of electron transport-inhibiting atrazine for realization of synergistic interaction with mesotrione was observed in the study of effectiveness of controlling *Cyperus esculentus* plants that are resistant to those herbicides (Armel et al., 2008).

Because of development and commercialization of new hydroxyphenyl pyruvate dioxygenase-inhibiting herbicide – tolypyralate, studies were conducted focused on determining its selectivity to maize and effectiveness of weed management (Kikugawa et al., 2015; Tonks et al., 2015; Metzger et al., 2018). Selectivity to maize depending on hybrid, rate and period of application, was also studied during combined use of tolypyralate with electron transport-inhibiting atrazine (Metzger et al., 2019). Mixtures of atrazine and tolypyralate, and also other hydroxyphenyl pyruvate dioxygenase inhibitors – isoxaflutole, mesotrione, topramezone, and tembotrione were used for control of multi-resistant biotype *A. tuberculatus*, resistant to 4 classes of herbicides: glyphosate, ALS-inhibiting herbicides, electron transport inhibitors and inhibitors of protoporphyrinogen oxidase. It was demonstrated that using those mixtures is an effective method to control this resistant biotype of weeds (Willemsse et al., 2021). Synergistic increase in the phytotoxic effect of using tolypyralate and atrazine produced effective control of dicotyledonous weeds *Amaranthus rudis* Sauer, *Ch. album* L., *Abutilon theophrasti* Medik, *Lamium amplexicaule* L., and grass weed *S. viridis* L. (Osipitan et al., 2018).

Use of mixtures of hydroxyphenyl pyruvate dioxygenase-inhibiting tolypyralate and ALS-inhibiting rimsulfuron, having increased the rate of application of rimsulfuron, was characterized by additivity interaction. This provides quite high efficiency of protection of maize crops and has advantages from the perspective of safety of the environment. However, using this mixture does not guarantee the high efficacy of controlling particular species of weeds that are resistant to mixture's constituents because of manifestations of antagonistic interaction. Mixture of tolypyralate with electron transport-inhibiting terbuthylazine is characterized by synergistic interaction, which produces high effectiveness of controlling a broad spectrum of species of weeds. The advantage of mixture of tolypyralate and terbuthylazine is that combination use of hydroxyphenyl pyruvate dioxygenase and electron transport inhibitors is a factor that can prevent emergence of weed biotypes that are resistant to ALS-inhibiting herbicides and in case of appearance of such biotypes is a means of combating them. This composition can completely satisfy needs of agriculture in combating resistant biotypes. Those conclusions are totally confirmed by the conducted analyses.

Conclusions

The results of the conducted studies revealed that high efficacy of protection of maize crops from weeds may be achieved by applying hydroxyphenyl pyruvate dioxygenase-inhibiting tolypyralate mixed with ALS-inhibiting rimsulfuron, as well as electron transport-inhibiting terbuthylazine. An obvious advantage of the mixture with rimsulfuron over the mixture with terbuthylazine is lower pesticide pressure on agrophytoecenes, since even doubled rate of application of rimsulfuron accounts only for 20 g, and the rate of application of terbuthylazine is 750 g of active substance per hectare. However, we should take into account that increasing the rate of applied ALS inhibitor allows general achievement of additive interaction during combination use with inhibitor of hydroxyphenyl pyruvate dioxygenase. But to certain weeds, antagonistic interaction may take place. In particular, antagonism in the mixture of tolypyralate and

rimsulfuron was observed in relation to *P. aviculare*, *V. arvensis* and *E. canadensis*. Antagonism is likely to occur in relation to weeds that are resistant to one of the mixture's component. Therefore, *P. aviculare* is resistant to rimsulfuron, and *V. arvensis* – to tolypyralate. Thus, in case of emergence of weeds resistant to ALS-inhibitors, we should take into account the possibility that the mixture of hydroxyphenyl pyruvate dioxygenase inhibitor and ALS inhibitor may not provide effective control of them due to antagonistic interaction. At the same time, when using tolypyralate in mixture with terbuthylazine, the interaction was synergistic. Study of intensity of fluorescence and formation of reactive oxygen species during influence of herbicides indicated that synergistic strengthening of phytotoxic action during combination use of inhibitors of hydroxyphenyl pyruvate dioxygenase and electron transport caused increase in the efficacy of blocking electron transport and intensity of formation of superoxide anion radical. Synergistic interaction in the mixture of tolypyralate and terbuthylazine provides high efficiency of controlling a broad range of weeds by this mixture, even if some species of those weeds are resistant to either tolypyralate or terbuthylazine alone.

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