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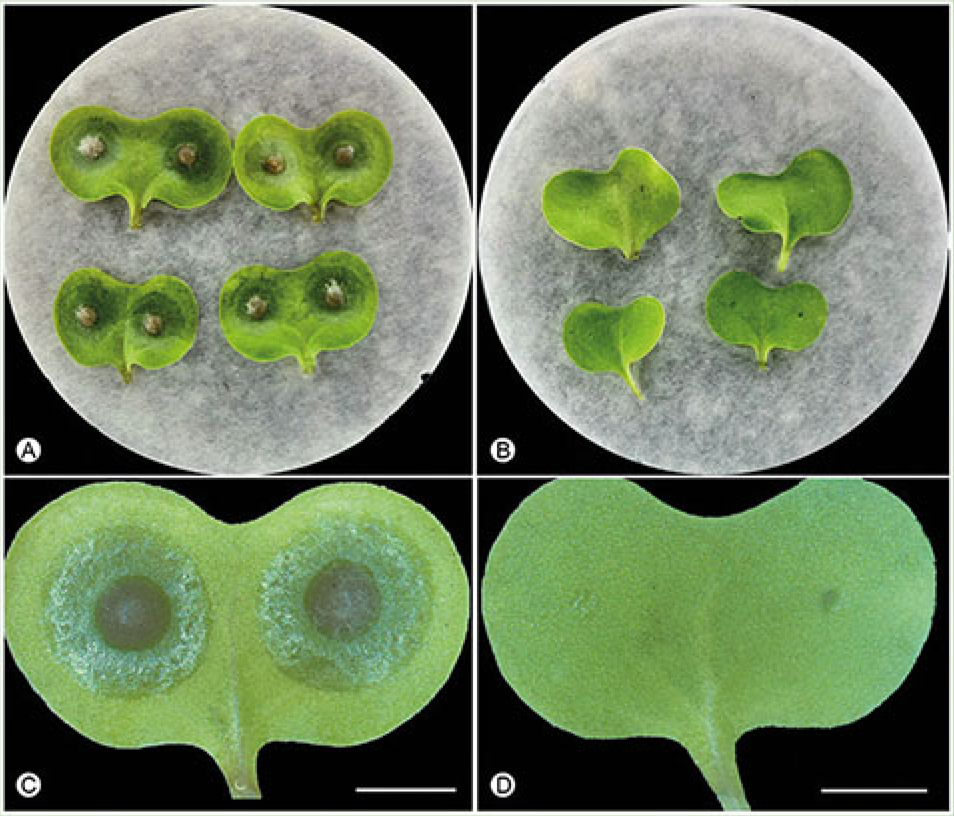

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Mini-review

DIRECTIONS FOR IMPROVEMENT OF THE HERBICIDE ASSORTMENT IN RUSSIA AT THE BEGINNING OF THE 21ST CENTURY

A.S. Golubev

All-Russian Institute of Plant Protection, St. Petersburg, Russia

e-mail: golubev100@mail.ru

Changes in herbicides recommended for the use in Russian Federation between 2000 and 2022 are analyzed. The main directions of iimproving chemical control of weeds are identified based on the integration of domestic market with the world market. Only a limited number of active ingredients was introduced in Russia during the last decade, including pinoxaden, thiencarbazone-methyl, piroxulam, sodium flucarbazone, topramezone, diclosulam, tembotrione, and metamifop. Improved formulations of herbicides such as colloidal solution concentrate with increased penetrability due to the particle size reduced by an order of magnitude became widely available. Premix herbicides were developed based on tribenuron-methyl, metsulfuron-methyl, florasulam, clopiralid, picloram, imazamox, imazapyr, imazethapyr, etc.Parameters for herbicide application were optimized to consider phenology of weeds. Novel technologies were implemented, such as growing hybrids resistant to certain active ingredients to allow their application during crop vegetation.

Keywords: herbicides, weeds, active ingredients, formulations, combined herbicides

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Introduction

Weeds are ubiquitous and persistent members of agricultural ecosystems, as opposed to the other harmful organisms, namely pests and plant disease agents, which become prevalent only in certain years when conditions are favorable for their development and spreading. Serious negative effects of weeds due to their competition with crops for light, water and mineral compounds are well known. In China, which is the largest pesticide manufacturer in the world, the herbicides add up to as much as one third of the total amount of the synthetic pesticides. While the production of insecticides is decreasing, there is an increasing trend in herbicide production (Jin et al., 2010).

Large scale application of herbicides in the second half of the 20th century facilitated the emergence of resistant weed populations, which made the researchers to seek alternative methods of weed control (Owen, 2016; Davis, Frisvold, 2017; Peterson et al., 2018; Gage, Schwartz-Lazaro, 2019; Beckie et al., 2019).The first instance of biological weed control was reported in 1971; since the end of the last century, researchers were enthusiastic by the development ofabout this approach (Umer et al., 2022). Unfortunately, the volumes of applied bioherbicides are still too low to be considered a success (Triolet et al., 2020). Still, we are optimistic about further advances in this field in the near future (Golubev, Berestetskiy, 2021). However, using of synthetic compounds to protect agricultural crops from unwanted plants remains the leading method of control.

The main trend in expanding the array of available herbicides at the early stages of chemical control was the search and commercialization of novel active ingredients with strong toxic action against weeds. Meanwhile, other factors associated with their application were not considered, leading to serious health problems in applicators, as well as in environmental contamination. Subsequently, the vector of development changed to aim at decreasing the application rates and the probability of negative side-effects on non-target objects (Umetsu, Shirai, 2020; Nagai, 2021).

Historically, the appearance of herbicides with novel mechanisms of action can be divided into the following stages (Umetsu, Shirai, 2020):

1) Before 1980. The discovery of auxin action of 2.4-D (2,4-dichlorophenoxyacetic acid) in 1942 was followed by the studies of herbicide activity of this molecule against the broadleaf plants. Between 1956 and 1975, the photosynthesis inhibitors were found belonging to the groups of urea, triazine and triazinone herbicides. In 1970, inhibitors of cell wall synthesis (dichlobenil), microtubule polymerization (trifluralin), etc, were discovered.

2) Between 1980 and 2000. In 1980, pyridazine was shown to distort carotenoid biosynthesis due to the inhibition of phytoen desaturase (PDS). From 1982 to 1986, glutamine synthase (GS) was proven to be affected by phosphinothricin, which is the active form of glufosinate and bialaphos. In 1986–89, the action of phthalimide herbicides onto protoporphyrinogen IX oxidase (PPO) was confirmed. In 1984, sulfonylurea and imidazolinone herbicides were shown to affect acetolactate synthase (ALS). In 1992–93, the target of triketone herbicide sulcotrione was proven to be 4-hydroxyphenylpyruvate dioxygenase (HPPD). Between 1993 and 2000, it was established that chloroacetamide affects very-long-chain fatty acid elongase (VLCFAE). Clomazone, which is the inhibitor of 1-deoxy-D-xylulose 5-phosphate (DXP) synthase in 2-C-methyl-D-erythritol 4-phosphate (MEP) pathway, was the last herbicide developed during that period. No herbicides with novel modes of action were reported during the following 30 years between the late 1980-s to 2017.

3) After 2018. During the last three years, information concerning three herbicides with novel mechanisms of actions and molecular targets became available. These include cinmethylin that interferes with fatty acid thioesterase (FAT), cyclopyrimorate that interferes with homogentisate solanesyltransferase (HST), and tetflupyrolimet that interferes with t dihydroorotate dehydrogenase (DHODH). With no doubt, this is an important milestone in the herbicide development, essential for suppression of herbicide-resistant weed biotypes in the future (Umetsu, Shirai, 2020).

Currently, in spite of remarkable amount of research of the last decade in the field of pesticide development with the use of modern break-through technologies, the introduction of new active ingredients into agricultural production remains infrequent (Kao-Kniffin et al., 2013; Umetsu, Shirai, 2020). At the same time, the global tendency of development of chemical plant protection means against weed is gradually changing from the search for novel active ingredients to the design of improved hi-tech formulations and combinations of ingredients proven to be effective, optimization of regulations (including the extension for period of application), and development of novel control technologies (including cultivation of genetically modified (GM) crops) (Nishimoto, 2019).

The goal of the present paper is the analysis of changes in the herbicide availability in Russia in 2000–2022 in the context of these changes.

Novel active ingredients

During the last decade, dozens of new herbicides with novel active compounds appeared all over the world. Most of them can be classified into the following groups according to their mechanism of action (Umetsu, Shirai, 2020):

1) inhibitors of ALS: propyrisulfuron (Sumitomo Chemical; Zeta-One®), metazosulfuron (Nissan Chemical; Altair®), pyrimisulfan (Kumiai Chemical; Best Partner®) and triafamone (Bayer; Council™ Complete). All of them are intended to protect rice (Sugiura et al., 2021).

2) inhibitors of HPPD: tefuryltrione (Bayer; Mighty-One®), enquinotrione (Kumiai Chemical; Effeeda®), ancotrione-sodium (Ishihara Sangyo Kaisha; Promise®), bicyclopyrone (Syngenta), tolpyralate (Ishihara Sangyo Kaisha; Brucia®). The three former and the two latter are for rice and maize, respectively (Yamamoto et al., 2021; Tsukamoto et al., 2021).

3) inhibitors of PPO: tiafenacil (Dongbu Hannong Chemical), trifludimoxazin (BASF; Tirexor™), cyclopyranil (Kyoyu Agri). These compounds are not in the market yet but the formulations are being developed by these companies.

4) inhibitors of VLCFAE: pyroxasulfone (Kumiai Chemical; Axeev®, Zidua®), ipfencarbazone (Hokko Chemical; Winner®, Fighter®), fenoxasulfone (Kumiai Chemical), dimesulfazet (Nissan Chemical). Pyroxasulfone is used to protect wheat, soya bean and maize, while the other three are for rice (Yamaji et al., 2014; Nakatani et al., 2016a; Nakatani et al., 2016b)

5) auxin-like herbicides: halauxifen-methyl (Dow - Corteva Agriscience; Arylex™) to protect cereals, and florpyrauxifen-benzyl (Corteva Agriscience; Rinskor™) to protect rice (Epp et al., 2016).

6) inhibitors of HST: cyclopyrimorate (Mitsui Chemicals Agro; Cyra®), devised for rice protection (Shino et al., 2018).

7) inhibitors of DHODH: tetflupyrolimet (FMC), used to protect rice (Dayan FE, 2019).

8) inhibitors of FAT: cinmethylin (BASF; Luximo™) against the weeds of cereal crops (Campe et al., 2018).

A safener designed in 2019 by Syngenta, named metcamifen, should also be mentioned. It is used in rice farming with herbicides based on clodinafop-propargyl (Brazier-Hicks et al., 2020; Umetsu, Shirai, 2020).

In Russian Federation, formulations on the basis of all these active ingredients are not allowed for industrial application yet, although many of them are the subject of intensive examination.

Among the herbicides that are currently registered for use in Russian Federation, as many as 8 active ingredients have been introduced in Russia during the last decade. Those were developed between 2000–10 and are commonly used around the world.

Pinoxaden (available in Russia since 2012) is combined with the safener cloquintocet-mexyl in such formulations as Axial, EC (45 g/l + 11.25 g/l), Axial 50, EC (50 g/l + 12.5 g/l) by Syngenta, and others. It destroys annual monocotyledonous weeds in the stands of grain crops, including the common windgrass *Apera spica-venti* (L.) Beauv., which is among the most harmful weeds (Artemyeva et al., 2021).

Thiencarbazone-methyl (2013) is included as one of several active ingredients in multiple premix herbicides by Bayer Crop Science AG. Some of them are recommended to be used in the maize stands: Maister power®, OD (31.5 g/l foramsulfuron + 1 g/l iodosulfuron-methylsodium + 10 g/l thiencarbazone-methyl + 15 g/l safener cyprosulfamide); Adengo®, SC (225 g/l isoxaflutole + 90 g/l thiencarbazone-methyl + 150 g/l safener cyprosulfamide); Capreno®, SC (345 g/l tembotrione + 68 g/l thiencarbazone-methyl + 134 g/l safener isoxadifen-ethyl) (Bagrinceva et al., 2015; Panfilov et al., 2015; Kashukoev et al., 2019). Others are applied to protect grain crops: Velocity, OD (10 g/l thiencarbazone-methyl + 60 g/l safener mefenpyr-diethyl); Velocity power, WDG (22.5 g/kg thiencarbazone-methyl + 11.3 g/kg iodosulfuron-methylsodium + 135 g/kg safener mefenpyr-diethyl); Velocity super, EC (80 g/l fenoxaprop-P-ethyl + 7.5 g/l thiencarbazone-methyl + 30 g/l safener mefenpyr-diethyl) (Golubev, 2018; Savva et al., 2021a). In 2020, the assortment was expanded by one other herbicide – Conviso® 1, OD (50 g/l foramsulfuron + 30 g/l thiencarbazone-methyl), which is intended for growing sugar beet hybrids resistant to this herbicide (see below).

Pyroxsulam (2013) is combined with the safener cloquintocet-mexyl in the herbicide Pallas 45, OD (45 g/l + 90 g/l) by Dow AgroSciences. It is used to control annual cereal and some dicotyledonous weeds in the stands of winter and spring wheat (Savva et al., 2014; Kalabashkina et al., 2020).

Flucarbazone-sodium (2013) is found in the herbicides Everest®, WDG (700 g/kg) by Arysta LifeScience и Kentavr, WDG (700 g/kg) by JSC «August» Inc. They are used in winter and spring wheat stands against annual grasses (common wild oat *Avena fatua* L., *A. spica-venti*, green foxtail *Setaria viridis* (L.) Beauv.) and some dicotyledonous weeds such as redroot pigweed *Amaranthus retroflexus* L., wild mustard *Sinapis arvensis* L., back bindweed *Fallopia convolvulus* (L.) A.

Love, shepherd's purse *Capsella bursa-pastoris* (L.) Medik., etc (Makhankova, Golubev, 2017; Osennij et al., 2018).

Topramezone (2014) is a component of the premix formulations by BASF SE, namely Stellar®, SL and Stellar® Plus, SL, contained 160 g/l dicamba и 50 g/l topramezone. They are used in maize stands against annual and some perennial dicotyledonous weeds, including those resistant to 2,4-D, as well as against some annual monocotyledonous weeds (Zbrailov et al., 2014).

Diclosulam (2020) is included into the herbicide Plector, WDG (750 g/kg) by JSC «August» Inc., which is recommended to control annual dicotyledonous plants in the soya bean stands (Golubev, 2021).

Tembotrione (2020) is combined with the safener isoxadifen-ethyl in the herbicide Laudis®, WDG (200 g/kg + 100 g/kg) and the premix formulation Capreno®, SC (345 g/l tembotrione + 134 g/l thiencarbazone-methyl + 68 g/l safener isoxadifen-ethyl) by Bayer Crop Science AG. These formulations are used in the maize stands to control annual and some perennial dicotyledonous and monocotyledonous weeds.

Metamifop (2020) is a part of the premix herbicide Nominee® Supreme, SE (100 g/l metamifop + 40 g/l bispyribac-sodium) by Kumiai Chemical Industry CO., LTD. It deserves special attention due to the problem of development of resistance in weeds of *Echinochloa spp.* to the herbicide Nominee®, SE in the rice fields of the Primorye Area (Lukacheva, Kostyuk, 2021a).

Besides the aforementioned compounds, pelargonic acid appeared in Russia as part of the formulation Mohoff, O/W EC (525 g/l) by JSC «August» Inc. Herbicides based on this active ingredient are used abroad in vineyards, potatoes, pumpkins, and several other crops, as well as paths in private gardens, against a wide range of unwanted plants, including the most notorious ones, such as the creeping thistle *Cirsium arvense* (L.) Scop., catchweed bedstraw *Galium aparine* L., etc. (Webber et al., 2014; Travlos et al., 2020; Alvarez et al., 2021; Ganji et al., 2022). In Russia, application of Mohoff is currently recommended only in the private lawns to combat mosses, lichens and unwanted grassy plants.

The list of synthetic herbicides available in Russian Federation was extended in in the last 20 years due to the inclusion of formulations based upon active ingredients discovered in the end of the 20th century, namely aclonifen fomesafen, diflufenican, flufenacet, amicarbazone, napropamide, pyraflufen-ethyl, prosulfocarb, prosulfuron, flumioxazine, foramsulfuron, cycloxydim, cyhalofop-butyl, ethametsulfuron-methyl (Spiglazova, Dolmatova, 2014; Hryukina, Naumov, 2016; Cherkashin et al., 2016; Bernaz, Polyakov 2020; Tkach et al., 2020; Morohovec et al., 2020; Bajrambekov et al., 2020; Morohovec et al., 2021; Lukacheva, Kostyuk 2021b; Devyatkin et al., 2021).

Novel types of formulations

One of the major principles of modern herbicide formulation design is the provision of fast penetration of the active ingredients in weeds. This concerns the substances applied both during crop vegetation (POST – post-emergence) and to the soil (PRE – pre-emergence and PPI – pre-plant incorporated) (Nandula, Vencill, 2015). To provide this possibility, formulators usually exploit adjuvants that are able to increase the efficacy of herbicides belonging to various chemical groups (Stagnari et al., 2007; Marcinkowska et al., 2018; Hao et al., 2019a; Hao et al., 2019b). As a result, adjuvants became widespread in the beginning of 21st century in Russia. In particular, they are crucial for the efficacy of glyphosate and sulfonylurea herbicides. The latter were no longer protected by the copyright, making them more affordable to end users. It is common to design a ready-to-use formulation, but it is not always feasible to integrate all the necessary additives and create a universal composition. Thus, it may be optimal to provide a basic formulation of a pesticide, while specific adjuvants are added in tank mixture depending upon the conditions (Makhankova, Dolgikh, 2020).

About 16 % of the total amount of the herbicides allowed to be used in Russian Federation are recommended in tank mixture with adjuvants as surface active agents (SAA). Nowadays, as many as 25 commercial names of SAA are registered on the basis of 9 active ingredients: isodecyl alcohol ethoxylate (Trend 90, L; ETD-90, L; Vivolt, L; Adyu, L; Satellit, L; Dar-90, L; Sigma-90, L; BIT 90, L; Styuart, L; Shans 90, L; Frend, L; LIP, L; PAV, L), the mixture of oil (fatty acid esters) and alkoxylated alcohols-phosphate esters (Dash®, EC), mixtures of mineral oil and fatty alcohols (Korvet, L), polyoxyethylene dodecyl ether (A-100, L), alkylethersulfate, sodium salt (Biopower, SL), ethoxylated monoalkylphenol (Neon 99, VSR; Neonol AF$_{9-12}$), fatty acid methyl ester mixtures (Amigo® star, EC; Fortuna, L), phosphate ester (Amigo®, SC; Khelper, SC; Miks, L), pinolene (MultIMastr, EC) (Makhankova, Dolgikh, 2020).Using many of these SAA strengthen herbicide action on certain weed species. Study by Makhankova et al. (2013) showed that addition of SAA Adyu, L to the herbicide Bomba, WDG is able to significantly increase the efficiency of treatment against *C. arvense* and *S. arvensis*.

Another way to facilitate penetration of active ingredients into a leaf is the design of innovative formulations. From a historical perspective, there are several phases of herbicide assortment optimization in this direction. Between 1960 and 1980, the main herbicide formulations applied in Russia were soluble powder (sodium salt 2,4-D, DNOC, sodium trichloroacetate), wettable powder (simazine, atrazine), emulsifiable concentrate (EC), water-soluble concentrate (treflan, zellek, fusilade), and water solutions (dialen, basagran).

In the end of the 20th century, alongside with the aforementioned forms, water dispersible granules (grodil, grasp), soluble granules (harmony), suspension concentrate (pyramin, butisan), and water glycol solution (kovboy, kross) were introduced (Petunova AA, Makhankova, 2009).The beginning of the 21st century was marked by appearance of colloid solution concentrate (CSC), oil emulsion concentrate (OEC), and oil dispersion (OD). These formulations are characterized by extremely high penetrability into plant tissue. Their particle sizes are by an order of magnitude smaller compared to classical formulations, such as EC. Notably, Russian crop protection companies could achieve sustainable success in this direction.

Schelkovo Agrohim JSC developed herbicide Betaren 22, containing 110 g/l desmedipham and 110 g/l phenmedipham, produced as an OEC. In Ryazan Province and Krasnodar Area, biological and economical efficacy of this herbicide was comparable to that of the standard (the same active ingredients in the form of the EC) and in Volgograd Province, it was even higher, while the active ingredient dosage was decreased by more than 30 % (Karakotov et al., 2015).

The same company also designed herbicide Benito containing 300 g/l bentazone in the form of the CSC. When applied under field conditions, it was more effective than the standard application of bentazone as water solution. This allowed decreasing the application rate of the active ingredient by 17.0–37.5 % without losing its efficacy (Golubev, 2019).

One of the interesting herbicides that appeared several years ago for household use is Roundup Gel, containing 7.2 g/l isopropylamine salt of the glyphosate acid. It was produced by the company "Monsanto" in the form of gel. Its distribution and application using a special applicator device improved convenience for the end user (Golubev et al., 2018a).

The need for improvement of the herbicide formulations can also be driven by new safety regulations. For instance, the use of organic solvents traditionally included into the EC became prohibited in the European countries due to stricter toxicological requirements, and this formulation is being replaced by the OD (Knowles, 2008; Gašić et al., 2015). In Russia, the herbicides in the form of OD also became widespread (Savva et al., 2021b; Savva et al., 2022).

Premix herbicides

Premix herbicide formulations that combine several active ingredients is one of the most efficient ways to expand the toolbox of available herbicides, especially in light of the extremely high costs of development, testing, and commercialization of novel active ingredients. That is why the majority of companies which do not belong to the transnational corporations chose this way, together with the design and improvement of herbicide formulations.

An alternative approach to benefit from the joint usage of several herbicides is preparation of a tank mixture prior to application under field conditions. This is, however, less convenient for a user and may cause unexpected antagonistic effects.

The main advantages of premix herbicides are:

1) Extended spectrum of activity due to combination of active ingredients with different mechanism of action (Larina, 2014; Savva et al., 2016; Telezhenko et al., 2019; Golubev, Borushko, 2020; Golubev, Borushko, 2021; Golubev, Chermenskaya, 2021). Experiments in winter wheat displayed a remarkable advantage of premix herbicide Spiker, EC (422 g/l dicamba + 18 g/l florasulam) over a single-compound standard Banvel, SL (480 g/l dicamba) in controlling flixweed *Descurainia sophia* (L.) Webb ex Prantl, common poppy *Papaver rhoeas* L., *F. convolvulus* (L.) A. Love, and *G. aparine* (Tokarev et al., 2016).

Applying combinations of different active ingredients is often helpful in overcoming the problem of herbicide resistanve. For instance, extensive use of isoproturon, clodinafop-propargyl, fenoxaprop-ethyl and sulfosulfuron against little seed canarygrass *Phalaris minor* Retz. in India facilitated the appearance and dispersal of resistant populations and made it necessary to explore the suitability of both the tank mixture (pendimethalin + metribuzin) and the ready-to-use premix herbicides based on mesosulfuron-methyl and iodosulfuron (Soni et al., 2021).

2) Increased efficacy of the treatment due to the synergistic interactions between the active ingredients in premix herbicides. For example, the study of susceptibility of perennial weeds, namely bindweed *Convolvulus arvensis* L. and field sowthistle *Sonchus arvensis* L. to the herbicide Kyleo, SL (240 g/l glyphosate + 160 g/l 2,4-D) Nufarm GmbH & Co KG allowed finding synergism between its active ingredients (Golubev et al., 2017). Noteworthy, similar tank mixtures glyphosate + 2,4-D or dicamba are applied in Canada against the common ragweed *Ambrosia artemisiifolia* L. due to the prevalence of weed populations resistant to glyphosate (Bae et al., 2017).

3) Decrease in negative side effects of each of the herbicide compounds on the environment. One such example is the premix herbicides based on sulfonylurea. Due to their high efficacy, low application rates, and high level of safety for the warm-blooded animals, herbicides of this group became prevalent in Russia at the border of the centuries (Makhankova et al., 2011). With time, however, the post-effect on the subsequent crops in the rotation due to prolonged decomposition in soil also became evident. Since the active ingredients are decomposed with different speed, those with the shorter half-life were used to partially substitute the compounds with the longer half-life. As a result, several combinations were designed such as Allay Light, VDG, containing 391 g/kg metsulfuron-methyl and 261 g/kg tribenuron-methyl, to decrease their residual effects on crops (Chernukha et al., 2011). That approach was common mainly in Russia and other former Soviet Union countries, but not in Western Europe.

Besides the sulfonylurea herbicides (amidosulfuron, metsulfuron-methyl, triasulfuron, chlorsulfuron, sulfometuron-methyl), other active ingredients such as clopyralid, picloram, imazamox, imazapyr, imazethapyr etc (Borushko et al., 2014; Stetsov, 2015; Kolupayev et al., 2019; Spiridonov et al., 2019; Saito et al., 2010) may also affect subsequent crops. Many of these compounds were exploited as the basis for effective premix herbicides (Spiridonov, Shestakov, 2013; Golubev et al., 2015; Dadayeva, Filonenko, 2016; (Makhankova et al., 2020).

It can also be noted that a combination of active ingredients may sometimes help decreasing both phytotoxicity for the crop under protection and residual effect throughout the crop rotation. One such example is Harmony Classic, WDG which is composed of thifensulfuron-methyl + chlorimuron-ethyl (Stetsov et al., 2018).

Extension of application period

As a rule, herbicide applications are recommended at the early stages of crop growth and development, or even before the seedlings' emergence because weeds at the early stages of their development are more susceptible to herbicides. Moreover, modern ideas concerning the planning of protective measures are based on the concept of critical timing of weed removal (CTWR) when treatments need to be applied to prevent yield decrease due to competition between the crop and weed plants (Nedeljković et al., 2021; Beiermann et al., 2022; Soltani et al., 2022). As a result, developmental stages have been established for each crop when they were routinely treated with herbicides. For example, before the end of the

20th century treatments of cereals with 2,4-D and dicamba were timed to the tillering because of susceptibility of these crops. As soon as the sulfonylurea herbicides appeared, the application period became extended and the treatments against dicotyledonous weeds were performed from the stage of 2–3 true leaves to the stage of stem extension (1–2 nodes) (Makhankova, Dolzhenko, 2013).

In spite of the fact that later treatments are generally considered to be less effective compared to the earlier treatments (Grzanka et al., 2022), in the beginning of 21st century the extension for application period tended to continue. An important aspect which started to attract attention of researchers was treatment timing tied to the phenology of late appearance of some weed species (Sadovnikova et al., 2021). The aim of such treatments is the avoidance of soil contamination with weed seeds after their maturation (Hill et al., 2016), which is critically important for preventing dispersal of resistant populations (Geddes, Davis, 2021).

The longest application period for a crop being safely protected by sulfonylurea herbicides was achieved with the appearance of the combined herbicide Caliber Gold, WDG from DuPont, containing 375 g/kg thifensulfuron-methyl and 375 g/kg tribenuron-methyl. This herbicide can be applied at one of the four growth stages of the cereal crops: 2–3 true leaves, tillering, stem extension (1–2 nodes), and the flag leaf. However, its application at the flag leaf stage has been found to be effective only when weather conditions didn't allow the timely treatment or when the perennial dicotyledonous weeds emerged late (Golubev et al., 2018b).

Late weed emergence necessitated a search for an herbicide with even broader application timing capabilities. As a consequence, Uniko, containing 100 g/l fluroxypyr и 2.5 g/l florasulam, was introduced by CSC Schelkovo Agrohim JSC. This premix can be applied even in the stage of heading (depending upon the susceptibility of the crop varieties) when *G. aparine* and *C. arvensis* dominate weed communities. This is especially important for the latter species when it germinates late and its most susceptible developmental stage coincides with the heading stage of the crop. Although weeds have already compromised the yield by the time of such a late treatment, their elimination would decrease yield losses and decrease weed seed bank in the field (Golubev et al., 2020).

Extension of the application period is also applicable in maize. It is common to treat this crop at the stage of 3–5 leaves when it is most vulnerable to the weed activity. For example, it was found in the experiments with Kelvin Plus, WDG (424 g/kg dicamba + 170 g/kg diflufenzopyr + 106 g/kg nicosulfuron) by BASF that later treatments (at the stage of 7–8 leaves) the weeds are more developed and resistant to the herbicide, so that the efficiency of protective measures is decreased. This is especially obvious in the cases of the lady's thumb *Persicaria maculosa* S.F. Grey, hedge-nettle betony *Stachys annua* L., and the velvet leaf *Abutilon theophrastii* Medik. Thus, late treatments make sense only when timely herbicide application could not be performed because of the weather, time constraints, and other interferences. It is also advisable to obtain data concerning susceptibility of the varieties and hybrids grown in particular regions to the herbicides applied (Golubev et al., 2021).

Novel technologies

The introduction of novel technologies of growing of genetically modified (GM) crops, which drastically changed the US agriculture, is dated back to 1996. Since then, the areas planted to GM crops keep on increasing, and so do the concerns of some researchers about safety of such approaches (Zimdahl, 2018; Nishimoto, 2019; Clark, Maselko, 2020; Bourdineaud, 2022). Without going into details of this criticism, the very fact of the development of these technologies is undoubtfully a remarkable milestone in plant protection from weeds (Brookes, 2014; Gosavi et al., 2022; Brunharo et al., 2022).

Unlike the US and some other countries, no GM hybrids resistant to glyphosate are grown in Russia. Nevertheless, since the beginning of the 21st century, the technologies of growing of special hybrids resistant to the two groups imidazolinone (sunflower, rapeseed) and sulfonylurea (sunflower) are used in Russia.

This approach allows suppressing both annual and perennial weeds. Premix herbicide Hermes, OD (50 g/l quizalofop-P-ethyl + 38 g/l imazamox) Schelkovo Agrohim JSC was tested in the stands of sunflower hybrid MAS 87 IR under the conditions of the Lower Volga region and suppressed annual, perennial and total weeds at the levels of 93–97 %, 84–87 %, and 93–97 %, respectively. The best results in terms of the yield increase were achieved when the herbicide was applied at the stage of 4 leaves, resulting in the yield increase of 0.84 t/ha (Spiridonov et al., 2017a).

Similarly, good efficacy was reported for the premix herbicide Ilion, OD (90 g/l clopyralid + 40 g/l imazamox) in the stands of spring rapeseed hybrids Salsa CL and Solar CL. In particular, weed suppression at the application rate of 0.8–1.2 l/ga reached 81.9–100 % and statistically significant rapeseed seed yield increase equaled to 74 % (Golubev, Zheltova, 2016).

Application of herbicide Express, WDG (750 g/kg tribenuron-methyl) in the rapeseed hybrid P 63 LE 10, resistant to this active ingredient, provided a decrease of weed infestation by 74–95 % within a month after the treatment. Again, the higher economic efficiency at the level of 0.1 t/ha was achieved by the application at the phase of 4 leaves (Spiridonov et al., 2017b).

Similar technologies are being developed abroad, including the application of imazamox against weeds in the stands of resistant varieties of sunflower, rapeseed and sorghum (Currie, Geier, 2021; Delchev, 2021).

Recently, growing the hybrid 4 K 446 of the sugar beet (*Beta vulgaris* L. ssp. *vulgaris* var. *saccharifera* Alef.), resistant to CONVISO ONE (50 g/l foramsulfuron + 30 g/l thiencarbazone-methyl) by Bayer was allowed in Russia. Similar approach, though exploiting the GM sugar beet hybrids, was used abroad in the beginning of the 21st century (Dewar et al., 2003). According to the experimental data obtained under the field conditions, the new technology CONVISO® SMART showed an advantage compared to the traditional approach that included treatments by herbicides in the betanal group. The main benefit was suppression of cereal weeds, primarily the cockspur *Echinochloa crus-galli* (L.) Beauv. Moreover, in contrast to the traditional scheme of sugar beet protection, the new technology allows suppressing devastating perennial dicotyledonous weeds (Golubev, Makhankova, 2022).

Conclusion

The analysis of changes in herbicides registered in Russia since the beginning of the 21st century indicates the prominent integration of the domestic market into the global herbicide market. As a consequence, the main trends were as follows:

1) Only a limited number of active ingredients was introduced in Russia during the last decade. On the other hand, it is extremely important for the Russian market that the new products are launched fast by the developers.

2) Herbicide formulations based on established active ingredients are constantly optimized and innovative technologies for their creation are used. The leading role of Russian companies should be mentioned in this respect.

3) Premix herbicides based on common active ingredients are developed. The latter two trends remain the main directions of new herbicide design by the Russian companies.

4) Optimal parameters of efficient herbicide application are defined with special attention to the weed phenology.

5) Novel technologies are adopted, including growing herbicide-resistant hybrids, thus allowing application of certain herbicides during crop vegetation period.

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Мини-обзор

ОСНОВНЫЕ НАПРАВЛЕНИЯ СОВЕРШЕНСТВОВАНИЯ АССОРТИМЕНТА ГЕРБИЦИДОВ В РОССИИ В НАЧАЛЕ 21 ВЕКА

А.С. Голубев

Всероссийский научно-исследовательский институт защиты растений, Санкт-Петербург

e-mail: golubev100@mail.ru

Анализ изменений ассортимента гербицидов, рекомендованных для использования в Российской Федерации с 2000 по 2022 годы, позволяет выявить основные направления его совершенствования, обусловленные глубокой интеграцией отечественного рынка химических средств защиты сельскохозяйственных культур от сорных растений в мировой рынок гербицидов: 1) появление небольшого количества новых действующих веществ гербицидов в последнее десятилетие: пиноксаден, тиенкарбазон-метил, пироксулам, флукарбазон натрия, топрамезон, диклосулам, темботрион, метамифоп; 2) совершенствование препаративных форм гербицидов и использование новых (в том числе, инновационных) технологий при их создании (концентрат коллоидного раствора (ККР), масляный концентрат эмульсии (МКЭ) и другие); 3) создание комбинированных препаратов на основе трибенурон-метила, метсульфурон-метила, флорасулама, клопиралида, пиклорама, имазамокса, имазапира, имазетапира и других; 4) определение оптимальных регламентов применения гербицидов с учетом фенологии развития сорных растений: обработки в фазу колошения зерновых при преобладании в посевах подмаренника цепкого и вьюнка полевого; 5) развитие новых технологий, таких как возделывание специальных гибридов, проявляющих устойчивость к действующим веществам гербицидов, что позволяет проводить обработку в период вегетации культуры.

Ключевые слова: гербициды, сорные растения, действующие вещества, препаративные формы, комбинированные препараты

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