Classification analysis of herbicides that were approved in 2018

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Abstract. An important area in agriculture is control of weeds. One of the effective ways to suppress weeds are herbicides. They are able to eliminate weeds, thereby increasing productivity of crops. There are a large number of herbicides that have been tested, registered and licensed. Each herbicide differs in the following criteria: chemical structure, herbicidal activity, mechanism of absorption and action, and ways of movement. Herbicides approved in 2018 are based on active substances which are described here. The active substances are diflufenopyr, flufenacet, flurtamone, bromoxynil, cycloxydim and some others. A classification was compiled for a visual study of herbicides. It is presented in this work with an indication of new herbicides that were approved for use in 2018.

1. Introduction

Currently, the control of weeds is one of the urgent problems of agriculture. There are two methods to protect crops, biological and chemical ones. Today, one of the main chemical methods is herbicides due to development of selective herbicides [1]. Now, the use of herbicides is an indispensable element of crop cultivation technology, because herbicides, due to certain components in their composition, are able to eliminate weeds, thereby increasing crop productivity [2].

According to the data of the Federal State Budgetary Institution “Russian Agricultural Center”, in total 65.05 thousand tons of pesticides were used in the territory of the Russian Federation in 2018; 63.48 thousand tons of plant protection chemicals were used, which amounted to 97.6% of the total used pesticides. Herbicides were most widely used pesticides as compared to other ones, as in previous years. In 2018, the consumption of herbicides amounted to 36.2 thousand tons, or 55.6% of the total pesticides. The followed herbicides were the most popular in 2018: Ballerina (1.59 thousand tons, the active substances are 2,4-D (2-ethylhexyl ether) and Florasulam, the manufacturer is “August”), Bazagran (1.27 thousand tons, the active substance is bentazone, the manufacturer is BASF), Tornado 500 (1.18 thousand tons, the active substance is glyphosate, the manufacturer is “August”), Total (1.1 thousand tons, the active substance is glyphosate, the manufacturer is Agro Expert Group), Sprut Extra (0.84 thousand tons, the active substance is glyphosate, the manufacturer is “Schelkovo Agrochem”). Herbicides demonstrated an average biological effectiveness of 86.3% in the Russian Federation. In 2018, the State catalog of pesticides and agrochemicals was replenished with new pesticides. In particular, 19 new herbicides were registered.

The present work is aimed to the analysis and classification of the active substances of herbicides
approved in 2018. It is possible to assess the diversity of some properties, such as action, safety and environmental friendliness of new herbicides based on the obtained data.

2. Results and discussion
This article provides a classification of herbicides. All active substances of herbicides differ in chemical structure, way of movement, herbicidal activity, as well as in the mechanisms of absorption and action (Table 1).

| Classification principles | Kinds | Active substance, Registration number CAS | Systematic name, IUPAC | Herbicides |
|---------------------------|-------|-------------------------------------------|------------------------|------------|
| Chemical structure        | aryloxyalkyl-carboxylic acids | 2,4-D 94-75-7             | (2,4-dichlorophenoxy) acetic acid | Ajkon, KE (AgroExpertGroup) |
|                           | benzoic acid derivatives      | Dicamba 1918-00-9         | 3,6-dichloro-o-anisic acid | Advokat, VR (Yunajtedhimprom) |
|                           | semicarbazones                | Diflufenopyr 109293-97-2  | 2-[(E)Z]-1-[3,5-difluorophenyl] semicarbazone methyl nicotinic acid | Kel’vin Plyus, VDG (BASF Corporation) |
|                           | oxyacetamides                 | Flufenacet 142459-58-3    | 4'-fluoro-N-isopropyl-2-[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yloxy] acetonilide | Artist, VDG (Bayer) |
|                           | pyridazine derivatives        | Flurtamone 96525-23-4     | (RS)-5-methylamino-2-phenyl-4-(α,α,α-trifluoromethyl)furan-3(2H)-one | Bakara Forte, KS (Bayer) |
|                           | cyclohexanediones             | Cycloxydim 101205-02-1    | (5RS)-2-[(E)Z]-1-(ethoxyimino)butyl]-3-hydroxy-5-[3(RS)-thian-3-yl)cyclohex-2-en-1-one | Stratos Ul’tra, KE (BASF Corporation) |
|                           | organophosphorus herbicides   | Glyphosate 1071-83-6      | N-(phosphonomethyl)glycine | Total VR (AgroExpertGroup) |
|                           | triazinones                  | Metamitron 41394-05-2     | 4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one | Rangoli-Metamitron (Rangoli) |
| Absorption mechanism      | through the leaves            | Dicamba 1918-00-9         | 3,6-dichloro-o-anisic acid | Advokat, VR; Diastart, VR |
|                           | through the roots             | Metamitron 41394-05-2     | 4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one | Malahit, VDG (Listerra) |
| Mechanism of action       | inhibitors of synthesis of amino acid | Glyphosate 1071-83-6    | N-(phosphonomethyl)glycine | Roundup, VR (Monsanto Europe S.A.) |
inhibitors of photosynthesis
Metamitron 41394-05-2
4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one
Marius KS (ZemlyakoFF)

inhibitors of synthesis of fatty acids
Cycloxydim 101205-02-1
(5RS)-2-[(EZ)-1-(ethoxyimino)butyl]-3-hydroxy-5-[(3RS)-thian-3-yl]cyclohex-2-en-1-one
Stratos Ultra, KE (BASF Corporation)

inhibitors of synthesis of pigments
Flurtamone 96525-23-4
(RS)-5-methylamino-2-phenyl-4-(α,α,α-trifluoro-m-tolyl)furan-3(2H)-one
Bakara Forte, KS (Bayer)

inhibitors of mitosis
Flufenacet 142459-58-3
4′-fluoro-N-isopropyl-2-[(trifluoromethyl)1,3,4-thiadiazol-2-yl] acetalide
Artist, VDG (Bayer)

hormone-like herbicides
Dicamba 1918-00-9
3,6-dichloro-o-anisic acid
Diastart, VR (Tekhnoeksport)

| Way of translocation | contact herbicides | systemic herbicides |
|----------------------|-------------------|-------------------|
| 2,4-D                | 94-75-7           | Ajkon Forte (AgroExpertGroup) |

Glyphosate 1071-83-6
N-(phosphonomethyl)glycine
Roundup, VR (Monsanto Europe S.A.)

The chemical classes of herbicides are divided into aryloxyalkylcarboxylic acids, derivatives of carbamic and thiocarbamic acids, derivatives of triazine, derivatives of benzoic acid, derivatives of sulfonylureas, derivatives of aryloxypropionic acids, derivatives of pyridazine, semicarbazones, oxyacetamides, cyclohexanediones triazines, organophosphorus herbicides and others. Each herbicide class has its own active ingredient [1].

The composition of the herbicides includes a wide amount of active substances. From year to year, new components are introduced into circulation. This fact is explained by systemic adaptation of weeds to the components of the preparations. So, it is necessary to create new plant protection products.

In 2018, herbicides based on the following active substances were developed, registered and approved for use. The active substances are diflufenzapyr, flufenacet, flurtamone, bromoxynil, cycloxydim and some others.

Flufenacet is a component of the herbicide Artist (Bayer) and Bakara Forte (Bayer). The second active substance of Bakara Forte is flurtamone. The composition of Stratos Ultra (BASF) includes cycloxydim as a component.

2,4-Dichlorophenoxyacetic acid (2,4-D) is one of the most widely used herbicides in the world. There is a lot of information about various cases of toxic effects of that chemical, and about its negative effects on human health. Fatal cases are known [3]. Herbicides based on 2,4-D belong to the II hazard class for humans and the III hazard class for bees [1]. Crop products and feed for farm animals sometimes contain quantities of 2,4-D that exceed the maximum permissible concentration [4]. The necessity to reduce the use of 2,4-D herbicidal compositions should be recognized.
Herbicides based on dicamba belong to the III hazard class for humans and the III hazard class for bees [1]. In soil, the movement of dicamba up and down depends on the movement of soil moisture. In the soil, it is destroyed relatively quickly. Bioconcentration Factor (BCF) of dicamba is 15 (low potential) [5].

Diflufenopyr is not persistent in the environment, it does not penetrate into groundwater, and it does not accumulate in the soil. It is one of the most rapidly degrading pesticides in the environment [6]. Acute oral toxicity LD50 for mammals is more than 5000 mg / kg. Acute dermal toxicity LD50 for mammals exceeds 5000 mg / kg. Diflufenopyr has an irritating effect on the mucous membrane of the eye. It belongs to the III hazard class for bees [7].

Flufenacet belongs to the III hazard class by acute oral and inhaled toxicities, but it belongs to the IV hazard class by dermal toxicity [8].

Flurtamone belongs to the III hazard class by acute oral and inhaled toxicities, and it belongs to the IV hazard class by dermal toxicity [9].

Acute oral toxicity LD50 of cycloxydim for rats is 3940 mg / kg, acute dermal toxicity LD50 for mammals is more than 2000 mg / kg, inhaled toxicity LD50 for mammals is more than 5 mg / kg. LD50 for bees is more than 100 μg / individual) [10].

Glyphosate-based herbicides belong to the III hazard class for humans and to the III hazard class for bees [1]. Glyphosate loses activity quickly in the soil. It does not accumulate in soil and water, it quickly transforms to elementary, naturally occurring substances such as carbon dioxide, phosphates, carbohydrates, amino acids [11]. It can accumulate in soil rich in organic matter, such as peaty soil [11].

Herbicides based on metamitron belong to the II hazard class for humans and to the III hazard class for bees [1]. Metamitron is relatively unstable in environment and decomposes relatively quickly with the formation of simple products that are not harmful to the environment [12].

Pesticides are one of the most toxic xenobiotics. They have high biological activity and they have a diverse effect on the biosphere. It expresses in the disruption of the interconnections of ecosystem components, the appearance of pesticide-resistant forms, and genetic disorders of cells. Pesticide residues pose a threat to the ecosystem, including humans. It is necessary to monitor the residual pesticides in environmental objects, and especially in the soil and food [13].

In the Russian Federation, monitoring of environmental pollution by residual amounts of pesticides is carried out within the framework of the Federal law "On environmental protection" by authorized Federal Executive bodies, including the Federal service for Hydrometeorology and environmental monitoring (Roshydromet) [11]. Modern high-precision chromatographic analysis methods are used to determine residual amounts [7, 8, 10, 11].

According to the mechanism of action, herbicides can be divided into the following classes: inhibitors of the synthesis of amino acids, photosynthesis inhibitors, lipid synthesis inhibitors, pigment synthesis inhibitors, meristematic mitosis inhibitors, membrane-destroying herbicides, and hormone-like herbicides and others [13].

The composition of hormone-like herbicides includes several chemical classes, such as aryloxyacarbonylic acids and their derivatives, and derivatives of benzoic acid [2].

The active substance that belongs to the class of aryloxyacarbonylic acids and their derivatives is 2, 4-D in the form of salt and ether. 2,4-D refers to phenoxyacetic acid derivatives. To date, 2,4-D is an ingredient in many herbicides [14]. In 2018, two trademarks of the herbicide manufactured by Agro Expert Group, LLC with this active substance were registered. Dicamba is the active substance that belongs to the class of derivatives of benzoic acid [15]. Dicamba can be assigned to the group of herbicides with auxin-like activity. External signs of dicamba damage include lengthening and curving of the lower part of the stem, curling and wilting of the leaves, and then their death [5]. Dicamba also became a part of two herbicides [1].

Inhibitors of amino acid synthesis include herbicides based on glyphosate, which refers to derivatives of phosphonoamino acids. Glyphosate is absorbed only through the leaves. Typical symptoms after the treatment of the plant are changes in the colour of leaf veins, death of the growth point, growth retardation of lateral shoots, and leaf chlorosis. Glyphosate has become one of the popular active
substances for inclusion in the composition of contact action herbicides. In 2018, nine herbicides based on it were registered [1].

The active substance metamitron, is a part of the herbicidal composition as an inhibitor of photosynthesis. In 2018 it became a component of three herbicides. These herbicides are intended for the treatment of vegetative parts of weeds [1].

According to the ability to move in the plant, the herbicides are divided into contact and systemic. Contact herbicides getting on the surface of a plant, cause damage at the point of contact. Systemic herbicides, on the contrary, after application penetrate into the plants and spread through the organs, causing a general lesion. Systemic herbicide especially well removes weeds with well-developed roots and other underground parts that are difficult to damage in other ways [1]. For example, glyphosate is a non-selective systemic herbicide. It is absorbed through the leaves, causing the death of both above-ground and underground organs of almost all plants with which it comes into contact. When glyphosate is degraded, a shorter molecule – aminomethylphosphonic acid (AMPA) is formed. It also has an herbicidal effect [11].

Analysis of various referenced has demonstrated that the production of herbicides is a promising direction in the field of agriculture. Based on the analysis of the above information, we can say that the task of creating of new products for their impact on weeds is being solved.

3. Conclusion
Developers and manufacturers strive to create a more effective herbicide. In 2018, their preference was given to inhibitors of the synthesis of amino acids, pigments, fatty acids, as well as to photosynthesis inhibitors, hormone-like herbicides, and mitosis inhibitors.

Herbicides that penetrate both roots and leaves are being developed. Systemic herbicides have a preference.

Developers and manufacturers strive to create the least environmentally hazardous herbicide. The active substances that are unstable in the environment, with low bioaccumulation and bioconcentration rates, mainly belonging to hazard class III, are mainly used.

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