Wiadomości Lekarskie

Original paper

Comparative hygienic assessment of the potential diquat hazard to the population when consuming agricultural crops treated with the Reglone Air 200 SL formulation using different application technologies (UAV, aerial, high-clearance rod sprayer treatment)

Keywords
plant protection, risk assessment, human health, environment

Abstract

Aim

Assessment of the hazard to the population when consuming treated crops by using different technologies.

Material and methods

Unmanned aerial vehicle XAG XPlanet 2020 equipped with four rotating rotors, which allows to keep in the air a 20-liter tank was used for spraying field; a manned aircraft AN-2 aggregated with a serial sprayer. High-clearance rod treatment of sunflower and rapeseed crops was carried out by using a PLA MAP II 2010 tractor.

Results

When the herbicide was applied by aerial application with UAV, the initial content of diquat dibromide in treated rapeseed and sunflower plants on the day of treatment was significantly higher than in the soil under crops ($p \leq 0.05$). The analysis of the diquat content dynamics in sunflower also showed a similar behavior of the a.i. in the plant after processing by another application methods: UAV, aerial and high-clearance rod treatment.
The integral index of hazard when using pesticide-contaminated products (IIHPCPC) = ADD+C+ DT50 = 4+1+1 = 6 points. That is why, diquat dibromide can be classified according to this index can be classified as compound of 3rd hazard class.

Conclusions

As a result of the conducted researches, it was established that the content of diquat in rapeseed and sunflower samples grown with the Reglone Air 200 SL application (after treatment and before harvesting) was below the maximum residue levels in those crops. There are no statistically significant differences in the behavior of diquat dibromide when applying by different methods of application (UAV, aerial, high-clearance rod treatment) in different agro-climatic zones of Ukraine.

Introduction. Plants occupy a special place in the migration chains of chemical plant protection products (CPPs). Since plants are an integral part of biota, they are closely related to other elements of the environment (water, soil, air). Plants are also capable of accumulation, especially perennial crops, and enzymatic degradation of pesticides [1, 2].

The integral principle of choosing plant protection methods in itself regulates the degree of negative impact of chemical agents on the ecosystem. When substantiating the chemical method, not only the biological and economic efficiency of the measures should be taken into account, but also the possibility of negative environmental consequences, which also have an economic price [2, 3, 4].

The study of the dynamics of the pesticides residue amounts in plants makes it possible to obtain a reliable quantitative and qualitative characteristic of the process using all experimental points of the dynamics; to quantitatively assess the influence of aggregate factors on the behavior of pesticides in the studied objects; to compare the results of research carried out in different conditions and with different objects, to predict the behavior of pesticides in plants.

Mechanization of the desiccation process is one of the key factors in increasing yield, work efficiency, and saving time and working forces [5, 6] in rapeseed and sunflower cultivation. Desiccation is a process of pre-harvest drying of plants with chemical formulations, which allows to speed up crop ripening by at least 5–10 days, partially destroy weeds, ensure uniform ripening, stop the spread of diseases and improve the quality of the grown crop [7].

However, in high density of crops such as cotton, the leaves usually overlap, so it is difficult to spray chemicals with traditional sprayers to ensure sufficient penetration of chemicals into the lower layers of cotton plants [8, 9]. It has been proven that aerial spraying is one of the most effective approaches to the chemicals application in plant protection [9, 10]. It provides rapid delivery of chemicals while reducing crop damage [11]. Unmanned aerial system (UAV) has great advantages of simple operation and good adaptation to the spraying environment, it has great potential for optimal spraying of pesticides according to the actual needs of the crop [12].

The aim: comparative hygienic assessment of the potential diquat hazard to the population when consuming agricultural crops treated with the Reglone Air 200 SL formulation using different application technologies (UAV, aerial, high-clearance rod sprayer treatment).

Materials and methods. Reglone Air 200 SL – one-component herbicide-desiccant of contact action. The active ingredient (a.i.) belongs to the dipyridylium derivatives. According to [13], diquat dibromide is characterized by rapid adsorption by green parts of plants and turning into hydrogen peroxide, which destroys cell membrane walls. This leads to rapid drying of the plant on which the formulation has fallen, too fast to ensure transfer to other parts of the plant. The herbicide interferes with cellular respiration, the process by which plants produce energy. Diquat dibromide decomposes on the surface of plants by photochemical degradation (Table I).

UAV. Field studies using the Reglone Air 200 SL were conducted in 2021. Processing of rapeseed and sunflower crops was carried out in the Kyiv region in accordance with the formulation consumption rate – 2.3 l/ha, working solution – 8 l/ha, spraying speed – 5.0 l/min. The total cultivated area was 5 hectares of sunflower and 2 hectares of rapeseed. Unmanned aerial vehicle (drone) XAG XPlanet 2020 equipped with four rotating rotors, which allows to keep in the air a 20-liter tank was used for spraying fields.

Aerial treatment. The introduction of the Reglone Air 200 SL formulation was carried out using a manned aircraft AN-2 aggregated with a serial sprayer in the Kherson region in 2012. Consumption rate – 2.3 l/ha, working solution – 25 l/ha, processing height 2-3 m above the crop. The total cultivated area: 2 hectares of sunflower and 2 hectares of rapeseed.

High-clearance rod treatment of sunflower and rapeseed crops was carried out in 2013 in the Kyiv region using a PLA MAP II 2010 tractor. Consumption rate – 2.3 l/ha, working solution – 300 l/ha, processing height 10-15 cm above the crop. The total cultivated area: 2 hectares of sunflower and 2 hectares of rapeseed.

Phase of rapeseed plants development at the treatment time: 87 BBCH, plant height – 70-80 cm. Phase sunflower plants of development at the time of processing:

Wiadomości Lekarskie

87 BBCH, plant height – 180 cm. Soil-climatic zone: forest-steppe, soils – gray podzolic.

All pesticide application procedures were carried out in the evening hours (after 7 PM) with minimal upward air currents, with air velocity not exceeding 2 m/sec, air temperature not higher than + 20ºC, relative humidity was in the range of 30-70%.

The study of the investigated chemical compound behavior was carried out using a specific hygienic method of natural experiment, sampling of plants – according to [14], starting from the first day of treatment and thereafter at equal intervals during the crop growing season until harvest. The study of the diquat dibromide residual amounts dynamics in the green mass of plants, rapeseed and sunflower seeds was carried out by chromatographic methods. Control samples were taken from plots where untreated crops of rapeseed and sunflower were grown.

The obtained results of the actual content of the studied a.i. in the soil, green mass of plants, rapeseed and sunflower seeds made it possible to calculate the constant of decomposition rate (k), half-life periods (DT_{50}) and almost complete decay (DT_{95}) in these objects using regression analysis methods. According to stability in plants, the substances were classified by [15].

The risk assessment for the population when using agricultural products grown in chemical protection systems (non-professional contingents) was carried out according to [16, 17], which involve the evaluation of the half-life (DT_{50}) in plants, the value of the acceptable daily dose (ADD) and the average daily consumption of the product on a four-gradation scale.

Statistical processing of the results was performed using the licensed statistical software package IBM SPSS Statistics Base v.22.

Results. The organoleptic properties of rapeseed and sunflower seeds (smell, color, appearance) at harvest in the treated samples did not differ from the control samples.

When the herbicide was applied from the air using a UAV, the initial content of diquat dibromide in treated rapeseed and sunflower plants on the day of treatment was significantly higher than in the soil under them ($p \leq 0.05$). This indicates the high efficiency of this type of processing and the relatively low level of environmental

Wiadomości Lekarskie

contamination. The concentration in the soil in all the studied samples was below the limit of quantitative determination of the method.

The analysis of the data presented in Table 2 shows that with all types of processing during the crop growing season, the content of diquat in rapeseed gradually decreased and after 7 days in the seeds was below the limits of quantification (LOQ) of the method. When harvesting the rapeseed crop, the content of diquat in the seeds was also below the LOQ of the corresponding method and did not exceed the maximum residue level (MRL) established for diquat in rapeseed – 0.4 mg/kg (the LOQ by the spectrophotometric method (SP) – 0.4 mg/kg), in rapeseed oil – 0.5 mg/kg (the LOQ of SF – 0.5 mg/kg).

The analysis of the diquat content dynamics in sunflower also showed a similar behavior of the a.i. in the plant during processing from a drone, aerial and high-clearance rod treatment. The concentration of diquat gradually decreased and after 6 days in the seeds was below the MRL. When harvesting the sunflower crop, the content of diquat in the seeds was below the LOQ of the corresponding method and did not exceed the MRL established for diquat in sunflower (seeds) – 0.5 mg/kg (LOQ of SF – 0.05 mg/kg), in sunflower oil – 0.1 mg/kg (LOQ of SF – 0.05 mg/kg).

The obtained results made it possible to substantiate the pre-harvest interval for sunflower – 6 days, rapeseed – 7 days.

The a.i. residual amounts in rapeseed and sunflower plants decreased at different rates. On average, on the 2nd day after treatment, the content of diquat dibromide in rapeseed was 3.4 times decreased ($p < 0.01$), 8 times ($p < 0.01$) on the 4th day and 9.3 ($p < 0.01$) times per 7 days compared to the initial concentration and was determined at or below the LOQ (Fig. 1). The concentration of diquat dibromide in sunflower during a similar time period decreased in plants more slowly (by 2 times on the second day compared to the initial content), and on the 4th day, significantly faster, by 9.4 times ($p < 0.01$) and by 14.5 ($p<0.01$) times on the 7th day compared to the initial concentration and was determined at the LOQ or below it (Fig. 2).

Mathematical processing of the results we obtained proved that the process of destruction of diquat dibromide obeys an exponential dependence. Based on the actual data of field experiment, we calculated the constant of decomposition rate (k), obtained

Wiadomości Lekarskie
equations describing the dependence of the concentration of the studied herbicide in rapeseed and sunflower plants from the moment of treatment. Since the differences in the k, DT_{50} and DT_{95} values are not reliable ($p>0.05$), we calculated their averaged values (Table II).

The next stage of this study was a comparative assessment of the risk to human health when consuming products grown after application of diquat dibromide in different ways.

Three main indices were evaluated on a 4-point scale:

1. the acceptable daily dose (ADD) of diquat dibromide is approved in Ukraine at the level of 0.002 mg/kg [20] that according to [16] gives 4 points;

2. DT_{50} in plants (for both sunflower and rapeseed) with different types of treatment did not differ reliably and in all cases did not exceed 5 days, i.e. it is estimated at 1 point;

3. there are no separate consumption norms (C) for sunflower seeds or sunflower oil, and rapeseed in Ukraine is mainly used as a technical crop and, quite a bit, is consumed in the form of oil, so we estimated the overall rate of oil consumption by the population of our country at 1 point (7,1 kg/person/year = 19.5 g/person/day).

Therefore, the integral index of hazard when using pesticide-contaminated products (IIHPCPC) = ADD+C+ DT_{50} = 4+1+1 = 6 points. That is, diquat dibromide can be classified according to this index as compound of 3rd hazard class (moderately hazardous compounds). In this case, the rather high toxicity of the pesticide (low value of ADD) is compensated by its low persistency in agricultural crops and the insignificant share of processed crops in the diet of Ukrainians. In addition, both studied crops undergo mechanical and often heat treatment before use, which leads to even greater destruction of diquat residues in them after processing.

Discussion. The data represented in Table 2 show that diquat dibromide quickly disappears from plant leaves in soil and climatic conditions of South-East Europe. According to the hygienic classification of pesticides by degree of hazard, according to persistency in vegetative agricultural plants diquat pertain to the 3rd class – moderately persistent.

It should also be noted that there are no statistically significant differences in the behavior of diquat dibromide after treatment with different application methods (UAV, aerial, high-clearance rod treatment) in agro-climatic zones of South-East Europe. And therefore, carrying out desiccation using a new method using a drone does not lead to a deterioration of the ecological situation in the region and does not increase the risk of a negative impact of diquat on non-professional contingents (consumers of agricultural products) and biocenoses. Considering the significant technological and economic advantages, convenience and efficiency of processing by this method, there is less risk of negative impact on agricultural workers (professional contingents) [8, 18, 19], the use of UAVs is very promising and will be actively and widely implemented in agricultural practice in the future.

It is important to note that the results of a comparative assessment of the risk to human health when consuming products grown after the pesticides application can vary depending on a set of factors, such as the dosage, application method, type of crop, and consumption rate [1, 4, 12].

Therefore, it is crucial to evaluate the specific context in which the pesticide is being used and its potential impact on human health and the environment. It is also important to consider the reliability and validity of the methods used to assess the risk and compare the results with other studies conducted in similar contexts [16, 17].

In this particular study, the risk associated with the application of diquat dibromide was evaluated using three main indices and was found to be moderate. The results suggest that the risk to human health when consuming products grown after the application of diquat dibromide in agro-climatic conditions of South-East Europe is relatively low due to the low persistence of the pesticide in agricultural crops and the small amount of processed crops in the diet of this region population [16, 17]. There are no statistically significant differences in the risk of products consumption grown after the application of a diquat dibromide after treatment with different application methods (UAV, aerial, high-clearance rod treatment). However, the use in different application technics of this pesticide and others should be monitored and evaluated to ensure safety and minimize any potential risks for population [2, 18, 19].

Conclusions:

Wiadomości Lekarskie

1. As a result of the conducted researches, it was established that the content of diquat in rapeseed and sunflower samples grown with the Reglone Air 200 SL application for 7 and 6 days, respectively, after treatment and before harvesting, was below the maximum residue levels in those crops. There are no statistically significant differences in the behavior of diquat dibromide when applying by different methods of application (UAV, aerial, high-clearance rod treatment) in different agro-climatic zones of Ukraine.

2. It was established that according to State Standard 8.8.1.002-98, diquat belongs to the 3rd hazard class – moderately stable compounds; by the value of the integral index of hazard when using pesticide-contaminated products, diquat dibromide can be classified as 3rd class (moderately hazardous compounds).

3. It is shown that treatment using UAVs does not lead to a deterioration of the ecological situation in the region and does not increase the risk of a negative impact of diquat on the population and environmental objects. Taking into account the above, as well as significant agro-economic advantages and greater safety for agricultural workers, the use of UAVs is very promising and will be actively and widely implemented in agricultural practice in the future, therefore this technology needs a comprehensive and detailed study from a hygienic point of view.

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Wiadomości Lekarskie

Table I

Basic physical and chemical properties of diquat

Physical and chemical properties	Diquat dibromide
CAS RN	34417-68-0
IUPAC Name	7,10-diazoniatricyclo[8.4.0.02,7]tetradeca -1(14),2,4,6,10,12-hexaene;dibromide
Empirical formula	$C_{12}H_{12}Br_2N_2$
Solubility in water, g/dm^3	700
Solubility in organic solvents, g/dm^3	in acetone, toluene, hexane – 0,1, in methanol – 25
Relative molecular weight	344.04
Coefficient n-octanol/water (20^{0}C)	log $K_{o/w}$ = - 4.60

Wiadomości Lekarskie

Table II

Diquat content in rapeseed and sunflower

Day after treatment	Diquat content (mg/kg)					
	UAV treatment		Aerial		High-clearance rod sprayer treatment	
	rapeseed	sunflower	rapeseed	sunflower	rapeseed	sunflower
Day of treatment	4,0±0,5 – pods	4,1±0,6 – baskets 0,73±0,01 – seed	3,2±0,5 – pods	2,9±0,5– baskets 0,65±0,01 - seed	3,8±0,3 – pods	3,6±0,2 – baskets 0,7±0,01 - seed
2	1,1±0,1 – pods	1,94±0,05 – baskets 0,66±0,02 – seed	0,95±0,2 – pods	1,3±0,2 – baskets 0,48±0,02 - seed	1,2±0,15 pods	2,1±0,05 – baskets 0,42±0,02 – seed
4	0,53±0,1 – pods	0,79±0,05 – baskets 0,50±0,01 – seed	0,4±0,1 – pods	0,26±0,05 baskets 0,1±0,01 - seed	0,45±0,15 – pods	0,32±0,1 – baskets 0,23±0,01 - seed
7 (harvest)	<0,4* - seed <0,5* - oil	0,28±0,01 - seed <0,05* - oil	<0,4* - seed <0,5* - oil	0,2±0,01 - seed <0,05* - oil	<0,4* - seed <0,5* - oil	0,25±0,01 – seed <0,05* - oil
k, day^{-1}	0,34±0,007	0,39±0,008	0,38±0,01	0,4±0,03	0,43±0,03	0,45±0,04
τ_{50}, day	2,04±0,04	1,78±0,04	1,75±0,13	1,67±0,1	1,59±0,14	1,69±0,1
τ_{95}, day	8,83±0,2	7,7±0,15	7,63±0,16	7,43±0,26	7,15±0,23	6,89±0,17

Notes: 1. "*" - below the limit of quantification of diquat in rapeseed – 0.4 mg/kg, oil – 0.5 mg/kg; in sunflower – 0.05 mg/kg, oil – 0.05 mg/kg; 2. in the control samples, diquat is below the limit of quantification of the method.

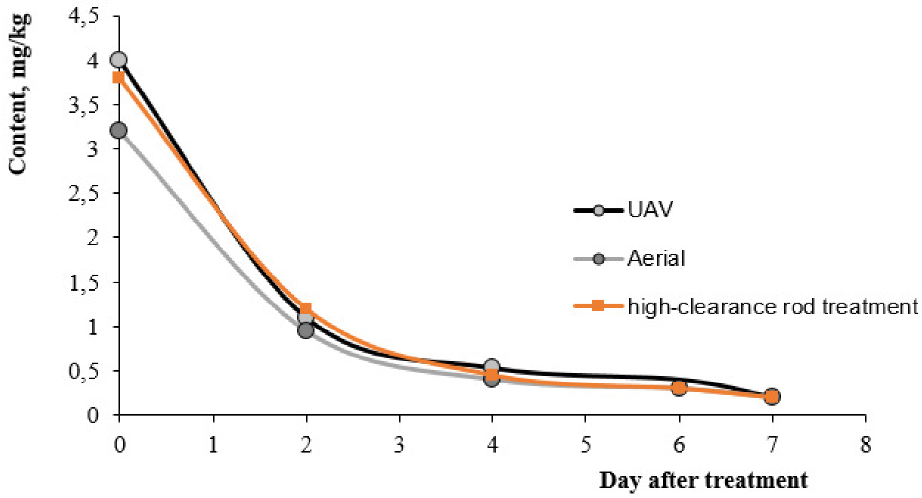
Content, mg/kg
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
0
1
2
3
4
5
6
7
8
Day after treatment
UAV
Aerial
high-clearance rod treatment

Figure 2
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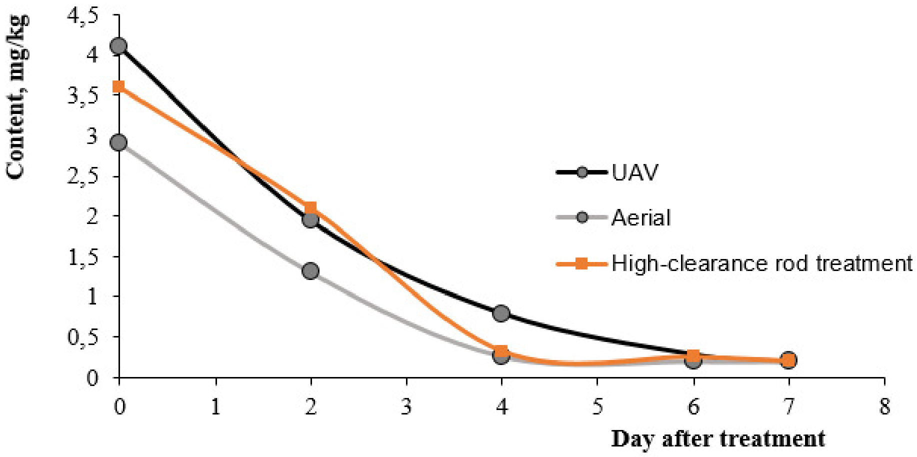
Wiadomości Lekarskie



Wiadomości Lekarskie

Table I - Basic physical and chemical properties of diquat

Table II - Diquat content in rapeseed and sunflower

Notes: 1. "*" - below the limit of quantification of diquat in rapeseed – 0.4 mg/kg, oil – 0.5 mg/kg; in sunflower – 0.05 mg/kg, oil – 0.05 mg/kg; 2. in the control samples, diquat is below the limit of quantification of the method.

Fig. 1 - Dynamics of diquat dibromide residual amounts in rapeseed after different types of treatment (UAV, aerial, high-clearance rod treatment)

Fig. 2. - Dynamics of diquat dibromide residual amounts in sunflower after different types of treatment (UAV, aerial, high-clearance rod treatment)