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HYGIENIC ASSESSMENT OF OCCUPATIONAL RISK FOR WORKERS DURING PRE- AND POST-EMERGENCE HERBICIDE TREATMENTS OF SUNFLOWER CROPS

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Abstract. Hygienic assessment of occupational risk for workers during pre- and post-emergence herbicide treatments of sunflower crops. Novokhatska O.O., Kondratiuk M.V., Grynzovskiy A.M., Pelo I.M., Babiienko V.V. Modern agriculture extensively uses pesticide formulations at various stages of crop growth. Sunflower cultivation accounts for 31% of the global production. Assessing the occupational risk associated with pesticide application in sunflower farming is of paramount importance. Improper handling and application of pesticide formulations can have immediate adverse effects on workers, leading to acute poisoning, long-term health consequences, and the potential for chronic illnesses, including neurotoxic effects. The aim of this study was to conduct a hygienic assessment of the professional risk faced by workers during pre- and post-emergence herbicide applications in sunflower cultivation. This assessment was carried out to establish the regulations for their safe usage. Research samples after the application of the herbicides AGAT, GARPUN, KORVUS, and PARUS (patches from overalls, gloves, skin swabs from exposed areas (face-neck, hands), air samples (atmospheric air, working zone and drift zone). The assessment of professional risk was conducted in accordance with the methodological recommendations provided by experts from the L.I. Medved's Research Center of Preventive Toxicology, Food and Chemical Safety, Ministry of Health, Ukraine (State Enterprise). Statistical analysis of the results was carried out using the licensed statistical software packages MedStat v.5.2 (Copyright© 2003-2019) and Microsoft® Excel® for Microsoft 365 MSO (Version 2305, Build 16.0.16501.20074). It has been determined that under real conditions, during pre- and post-emergence herbicide applications in sunflower cultivation using AGAT, GARPUN, KORVUS, PARUS preparations, while adhering to recommended agrotechnical and hygiene safety regulations, the inhalation, dermal, complex, and combined (AGAT and PARUS) risks for applicators are 0.0409±0.0179, 0.0429±0.0193, 0.0838±0.0224, and 0.1557±0.1322 a.u., respectively, and for tractor operators – 0.0818±0.0358, 0.0425±0.0192, 0.1243±0.0356, and 0.2347±0.1567 a.u., respectively. There is no observed increase in hygiene standards in the workplace atmosphere and in the air of the potential drift zone. It has been proven that the professional risk of their use does not exceed permissible limits (<1). It has been determined that during the performance of technological operations, the mentioned risks in applicators and tractor operators did not differ significantly ($p>0.05$). However, a significant difference was found in the proportion of percutaneous risk (42.7±17.4% in applicators compared to 34.8±17.0% in tractor operators; $p=0.034$). The regulations for the safe use of the investigated pesticide formulations have been substantiated. Statistical analysis of the obtained results revealed that the values of inhalation, dermal, and combined risks during the application of these pesticides did not significantly differ during the various technological operations (applicators and tractor operators) ($p>0.05$). The values of the combined comprehensive risk associated with the use of the studied preparations also did not show significant differences ($p>0.05$). The proportion of dermal risk was significantly higher in applicators compared to this parameter determined in tractor operators ($p=0.034$).

Реферат. Гігієнічна оцінка професійного ризику для працівників при виконанні до-, післясходових обробок гербіцидами посівів соняшника. Новохацька О.О., Кондратиук М.В., Гринзовський А.М., Пельо І.М., Бабієнко В.В. У сучасному сільському господарстві широко застосовуються пестицидні формуляції на різних етапах вегетації культури. Виробництво соняшника становить 31% від світового об'єму. Оцінка професійного

ризиком при застосуванні пестицидів на соняшнику є важливим завданням. Безпосередній вплив пестицидних формуляцій на працівників при недотриманні регламентів застосування може викликати гостре отруєння, мати віддалені наслідки та призвести до хронічних захворювань (нейротоксичні ефекти). Метою роботи була гігієнічна оцінка професійного ризику для працівників при виконанні до- або післясходових обробок гербіцидами посівів соняшника для обґрунтування регламентів їх безпечного використання. Дослідні зразки після застосування гербіцидів АГАТ, ГАРПУН, КОРВУС та ПАРУС (нашивки зі спецодягу, рукавички, змиви з відкритих ділянок шкіри (лице-шия, кисті рук), проби повітря (атмосферного, робочої зони та із зони знесення). Оцінювання професійного ризику здійснювали згідно з методичними рекомендаціями, запропонованими фахівцями Наукового центру превентивної токсикології, харчової та хімічної безпеки ім. Л.І. Медведя. Статистичну обробку результатів проводили з використанням пакету ліцензійних статистичних програм MedStat v.5.2 (Copyright© 2003-2019) та Microsoft® Excel® для Microsoft 365 MSO (версія 2305 збірка 16.0.16501.20074). Установлено, що в реальних умовах при виконанні до- або післясходових обробок гербіцидами посівів соняшника препаратами АГАТ, ГАРПУН, КОРВУС та ПАРУС при дотриманні рекомендованих агротехнічних і гігієнічних регламентів безпечного застосування інгаляційний, перкутанний, комплексний та комбінований (АГАТ і ПАРУС) ризику для заправників становлять $0,0409 \pm 0,0179$, $0,0429 \pm 0,0193$, $0,0838 \pm 0,0224$ та $0,1557 \pm 0,1322$ у.о. відповідно, а для трактористів – $0,0818 \pm 0,0358$, $0,0425 \pm 0,0192$, $0,1243 \pm 0,0356$ та $0,2347 \pm 0,1567$ відповідно; не спостерігається підвищення гігієнічних нормативів у повітрі робочої зони та повітрі зони можливого знесення та доведено, що професійний ризик при їх використанні не перевищує допустимий (<1). Визначено, що під час виконання технологічних операцій вищезазначені ризику в заправників та трактористів достовірно не відрізнялись ($p > 0,05$), проте виявлено достовірну відмінність у частці перкутанного ризику ($42,7 \pm 17,4\%$ у заправників проти $34,8 \pm 17,0\%$ у трактористів; $p = 0,034$). Обґрунтовано регламенти безпечного застосування досліджуваних пестицидних формуляцій. Статистичний аналіз одержаних результатів показав, що величини інгаляційного, перкутанного та комплексного ризиків під час застосування запропонованих до вивчення препаративних форм достовірно не відрізнялися в ході проведення різних технологічних операцій (заправників та трактористів) ($p > 0,05$). Величини комбінованого комплексного ризику застосування досліджуваних препаратів також достовірно не відрізнялися ($p > 0,05$). Частка перкутанного ризику була достовірно вищою в заправників порівняно з цим показником, що визначався в трактористів ($p = 0,034$).

Modern agriculture widely employs pesticide formulations at various stages of crop growth. The high percentage of the global population suffering from food scarcity necessitates an increase in food production, which demands more intensive agricultural practices [1, 2]. Ukraine is a global leader in agribusiness, and notably, sunflower production has reached record-breaking levels in the country, accounting for 17.5 million tons or 31% of the global volume [3]. The key to achieving high crop yields lies in the application of pesticides at different stages of crop cultivation.

To prevent the negative impact of pesticides on the health of workers, modern methodologies for assessing professional risk are employed [6, 7, 8, 9].

The assessment of professional risk in the application of pesticides in sunflower cultivation is a crucial task. The direct impact of pesticide formulations on workers, when regulatory guidelines are not followed, can lead to acute poisoning, have long-term consequences, and result in chronic illnesses, including neurotoxic effects [4, 5].

The highest risk indicators are determined using the methodology proposed by experts from the L.I. Medved's Research Center of Preventive Toxicology, Food and Chemical Safety, Ministry of Health [10].

It is important to note that the use of combined pesticide formulations may lead to the exceedance of permissible levels of professional risk, necessitating the implementation of preventive measures to mitigate the hazardous effects of pesticides on workers [11].

The aim of this study was to conduct a hygienic assessment of the professional risk faced by workers during pre- and post-emergence herbicide applications, including AGAT, GARPUN, KORVUS, and PARUS in sunflower cultivation. This assessment was carried out to establish the regulations for their safe usage.

MATERIALS AND METHODS OF RESEARCH

Field studies on the working conditions of employees (applicators and tractor operators) during the application of the studied pesticides were conducted in the Zhytomyr region, which is characterized by the soil and climatic conditions of the Ukrainian Polissya region. The conditions of pesticide formulation application are detailed in Table 1.

Research was approved by the Commission on Bioethical Expertise and Ethics of Scientific Research of the Bogomolets National Medical University, protocol No. 179 dated November 27, 2023.

The treatment with the studied preparations was carried out using a boom sprayer OPSh-2000, which was mounted on a MTZ-82 tractor.

The preparation of the working solution of the pesticides was performed by the applicator, and the duration of this operation was 10 minutes. The sunflower crop treatment was conducted by the tractor operator and took 20 minutes. Both the applicator and the tractor operator wore specialized protective clothing, including a synthetic fabric jumpsuit and boots. They also used rubber gloves and respirators as personal protective equipment.

Table 1

Conditions of application of the studied herbicides on sunflower

Pesticide formulations	Active ingredient (AI), content of AI in the formulation	Maximum recommended dosage of the product	Rate of working fluid consumption
AGAT	imazamox, 33 g/l imazapyr, 15 g/l	1.2 l/ha	250 l/ha
GARPUN	tribenuron-methyl, 758 g/kg	30.0 l/ha	300 l/ha
KORVUS	propisochlor, 720 g/l	30.0 l/ha	300 l/ha
PARUS	S-metolachlor, 312.5 g/l terbuthylazine, 187.5 g/l	4.5 l/ha	200 l/ha

Air sampling during the refilling of the sprayer, inside the tractor cabin, and in the treated area was conducted using a portable two-channel electric aspirator EA-2-20.

Air samples were collected on "blue tape" paper filters and silica gel. During each work operation, three samples were sequentially taken at one point. Research on the presence of pesticides on the skin of workers was conducted after completing the operations using degreased and water-diluted ethyl alcohol, in a 1:1 ratio, along with cotton swabs. The patch method was also employed on specialized clothing: three-layer patches

(outer layer – cotton fabric, middle layer – medical gauze, inner layer – "blue tape" filter).

The sampling of samples and the quantitative determination of the content of active substances in the air of the working zone, atmospheric air, swabs from exposed skin surfaces and gloves, and patches on the workers' specialized clothing were carried out using high-performance liquid and gas-liquid chromatography methods.

The limits of quantitative determination, hygiene standards, and methods for investigating the active substances are provided in Table 2.

Table 2

Hygiene standards and limits of quantitative determination of the studied active substances in the air of the working zone, atmospheric air, swabs from the skin surface, patches from the specialized clothing of personnel, and soil

Active ingredient	Working zone air, mg/m ³		Atmospheric air, mg/m ³		Swabs, patches, mg	Soil, mg/kg		Method
	MAC/TSEL	LOQ [No. MI]	MAC/TSEL	LOQ [No. MI]	LOQ	TAC/MAC	LOQ [No. MI]	
imazamox	/1.0	0.5 [649-2006]	/0.04	0.03 [649-2006]	0.002	0.4/	0.1 [650-2006]	HPLC
imazapyr	/1.0	0.017 [6239-91]	/0.5	0.025 [411-2003]	0.001	/0.03 (water migration)	0.03 [722-2007]	HPLC
tribenuron-methyl	/0.1	0.01 [6090-91]	/0.003	0.002 [353-2002]	0.001	0.01/	0.005 [6076-91]	HPLC/GLC
propisochlor	/1.0	0.5 [892-2009]	/0.01	0.008 [892-2009]	0.002	0.6/	0.06 [891-2009]	GLC
S-metolachlor	/0.5	0.5 [168-99]	/0.02	0.01 [168-99]	0.002	0.02/	0.02 [795-2007]	GLC
terbuthylazine	/1.0	0.02 [2869-83]	/0.05	0.04 [635-2006]	0.002	0.04/	0.01 [1328-76]	GLC

Notes: MAC – maximum allowable concentration; TAC – tentatively allowable concentration; TSEL – tentatively safe exposure levels; LOQ – limit of quantitation; MI – methodological instructions; HPLC – high-performance liquid chromatography; GLC – gas-liquid chromatography.

The assessment of professional risk was conducted in accordance with the methodological recommendations [10]. Considering that most of the studied pesticide formulations are combined, there is a possibility of simultaneous action of multiple active substances. Therefore, to assess the professional risk, we calculated the risk values when multiple active substances are present within one formulation. The combined risk was determined by simply summing the risk values of several active substances when they are encountered together (complex intake) [12].

Statistical analysis of the results was carried out using the licensed statistical software packages MedStat v.5.2 (Copyright© 2003-2019) and Microsoft® Excel® for Microsoft 365 MSO (Version 2305 Build 12.0.6425.1000, 2007) (License Identifier: CWW_0071e48a-250c-4bdb-9013-b8daf357b5e9_b5685e92-c95d-4399-9b83-449d76a26fb6_79f3b2da2f9adcda29). The normality of the samples was assessed using the W Shapiro-Wilk criterion, and it was determined that all exper-

imental series followed a normal distribution (W=ranging from 0.873 to 0.962). Based on this, the t-Student criterion was selected for comparison [13, 14]. During the study, the samples underwent the following statistical analysis: determination of the mean value and standard error of the mean, variance of the samples, standard deviation, and calculation of the proportion. The level of statistical significance was set at 80% at a significance level of 0.05.

RESULTS AND DISCUSSION

The results of the conducted field studies on the working conditions of employees during the implementation of production operations involving the use of pesticides showed that all active substances of the studied pesticide formulations in the air of the working zone were detected in quantities below the limit of quantitative determination of the respective analytical methods (Table 3). The obtained data indicate the absence of violations of hygiene standards in the working zone air for these active substances (Table 2).

Table 3

Content of active substances of the investigated pesticides in air samples during their application for sunflower protection, mg/m³ (M±m, n=3)

Pesticide formulations	Active ingredient	Air in the breathing zone		Air in the treatment zone after			Air in the potential drift zone** after			Soil of the area after		
		applicator	tractor operator	1 hour	3 days	7 days	1 hour	3 days	7 days	1 hour	3 days	7 days
AGAT	imazamox	<0.5*	<0.5*	<0.5*	<0.5*	<0.5*	<0.03*	<0.03*	<0.03*	<0.1*	<0.1*	<0.1*
	imazapyr	<0.017*	<0.017*	<0.017*	<0.017*	<0.017*	<0.025*	<0.025*	<0.025*	<0.03*	<0.03*	<0.03*
GARPUN	tribenuron-methyl	<0.01*	<0.01*	<0.01*	<0.01*	<0.01*	<0.002*	<0.002*	<0.002*	0.16±0.01	0.051±0.008	-
KORVUS	propisochlor	<0.5*	<0.5*	<0.5*	<0.5*	<0.5*	<0.008*	<0.008*	<0.008*	7.9±0.1	5.1±0.1	-
PARUS	S-metolachlor	<0.5*	<0.5*	<0.5*	<0.5*	<0.5*	<0.01*	<0.01*	<0.01*	1.96±0.34	1.3±0.2	0.31±0.04
	terbuthylazine	<0.02*	<0.02*	<0.02*	<0.02*	<0.02*	<0.04*	<0.04*	<0.04*	0.82±0.15	0.69±0.09	0.23±0.02

Notes: * – below the limit of quantitative determination of the methods in the working zone air and atmospheric air; ** – the study was conducted at a distance of 300 meters from the edge of the plot.

Analysis of the content of active substances in swabs from exposed skin surfaces and patches on the specialized clothing of personnel was conducted (Table 4). Only the contamination of the applicator's rubber gloves with propryzamide amounted to 0.0056 mg.

On the exposed skin areas of workers (face, neck) and on the skin surface of their hands under the

gloves, the studied pesticides were below the limit of quantitative determination of the respective methods. All active substances in the patches of the applicator and tractor operator were below the limit of quantitative determination of the methods.



Table 4

Content of active substances in swabs from the surface of exposed skin areas and patches on the workwear of workers during the application of pesticides for sunflower protection

Pesticide formulations	Active ingredient	Swabs from all areas, mg **			Patches on workwear, mg/dm ²			
		applicator		tractor operator	applicator		tractor operator	
		face, neck, and hands	gloves	face, neck, and hands	headgear, chest, shoulders, forearms	back, thighs, calves	headgear, chest, shoulders, forearms	back, thighs, calves
AGAT	imazamox	<0.002*	<0.002*	<0.002*	<0.002*	<0.002*	<0.002*	<0.002*
	imazapyr	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*
GARPUN	tribenuron-methyl	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*	<0.001*
KORVUS	propisochlor	<0.002*	0.0056	<0.002*	<0.002*	<0.002*	<0.002*	<0.002*
PARUS	S-metolachlor	<0.002*	<0.002*	<0.002*	<0.002*	<0.002*	<0.002*	<0.002*
	terbuthylazine	<0.002*	<0.002*	<0.002*	<0.002*	<0.002*	<0.002*	<0.002*

Notes: * – below the Limit of Quantitative determination of the methods; ** – swabs were collected from the entire surface of the open areas of the workers' bodies; Surface area, dm²: Face – 6.5; Neck – 2.6; Shoulders – 29.1; Forearms – 12.1; Hands – 8.2; Chest – 35.5; Back – 35.5; Thighs – 38.2; Calves – 23.8.

The obtained factual data on the assessment of workers' working conditions allowed us to calculate the professional risk for the complex exposure (through the skin and respiratory tract) and for the combined effect of multiple active substances within one formulation (Table 5). An analysis of the results of the calculated professional risk for combined and complex effects of the studied active substances showed that in all cases, it is permissible (less than 1). There were no significant differences in risk values between different exposure routes and their combined and complex effects on workers. Likewise, there were no significant differences in these values among workers performing different types of tasks (applicators when preparing pesticide solutions, tractor operators during treatments) based on the Student's criterion ($p > 0.05$). The proportion of percutaneous risk in applicators and tractor operators averaged $42.7 \pm 17.4\%$ and $34.8 \pm 17.0\%$, respectively.

Statistical analysis of the obtained results showed that the values of inhalation risk were higher in tractor operators (0.0818 ± 0.0358) compared to applicators (0.0409 ± 0.0179), but this difference was not statistically significant ($p = 0.054$ according to the Student's criterion). The values of percutaneous risk for workers involved in different technological operations were similar and did not significantly differ ($p = 0.056$ according to the Student's criterion), with

values of 0.0429 ± 0.0193 and 0.0425 ± 0.0192 for applicators and tractor operators, respectively. The complex risk, on average, was higher in tractor operators than in applicators, with values of 0.1243 ± 0.0356 and 0.0838 ± 0.0224 , respectively, but this difference was not statistically significant ($p = 0.057$ according to the Student's criterion).

The values of professional risk during the use of combined pesticide formulations did not exceed the permissible limit (less than 1). The combined risk values for applicators averaged 0.1557 ± 0.1322 , while for tractor operators, it averaged 0.2347 ± 0.1567 arbitrary units.

The analysis of air samples in the zone of potential exposure showed that the content of the investigated active substances in pesticide formulations did not exceed the established hygiene standards in the atmospheric air (Table 3).

The dynamics of the content of the studied pesticides in the soil of the treated area 1 hour, 3 days, and 7 days after the treatments indicated the rapid disappearance of their active substances from the soil.

The obtained results allowed for the justification of safety regulations for the use of the investigated preparations AGAT, GARPUN, KORVUS, and PARUS in sunflower cultivation in the agro-industrial complex of Ukraine (timing of workers' entry into treated areas).

Table 5

Values of potential risk of hazardous effects of pesticides on applicators and tractor operators during the application of pesticides for sunflower crop protection

Pesticide formulations	Active ingredient	Risk values								Dermal risk fraction, %	
		inhalation		dermal		complex		combined		A *	T
		A	T	A	T	A	T	A	T		
AGAT, SL	imazamox	0.0598± 0.0129	0.1195± 0.0257	0.0001± 0.000	0.0001± 0.000	0.0599± 0.0129	0.1196± 0.0258	0.0622	0.1239	0.24	0.12
	imazapyr	0.002± 0.0004	0.0041± 0.0009	0.0002± 0.000	0.0002± 0.000	0.0023± 0.0005	0.0043± 0.0009			9.72	5.07
GARPUN 750, WG	tribenuron-methyl	0.0143± 0.0031	0.0287± 0.0062	0.0525± 0.0113	0.0521± 0.0112	0.0668± 0.0144	0.0808± 0.0174	-	-	78.54	64.5
KORVUS, EC	propisochlor	0.0717± 0.0154	0.1434± 0.0309	0.0531± 0.0114	0.0521± 0.0112	0.1248± 0.0269	0.1955± 0.0421	-	-	42.56	26.65
PARUS 500, SC	S-metolachlor	0.0956± 0.0206	0.1912± 0.0412	0.0350± 0.0075	0.0347± 0.0075	0.1306± 0.0281	0.2259± 0.0487	0.2491	0.3455	26.79	15.37
	terbuthylazine	0.0019± 0.0004	0.0038± 0.0008	0.1166± 0.0251	0.1158± 0.0249	0.1185± 0.0255	0.1196± 0.0258			98.39	96.8
Shapiro-Wilk criterion W		0.873	0.874	0.892	0.890	0.881	0.962	-	-	0.933	0.878
Risk values, M±m, arbitrary units		0.0409± 0.0179	0.0818± 0.0358	0.0429± 0.0193	0.0425± 0.0192	0.0838± 0.0224	0.1243± 0.0356	0.1557± 0.1322	0.2347± 0.1567	42.7± 17.4	34.8± 17.0
Comparison of related samples at df=5 (p=)		0.054		0.056		0.057		-		0.034*	

Notes: A – applicator; T – tractor operator; * – dermal risk fraction is significantly higher in applicators compared to tractor operators; M±m – mean and standard error of the mean; a.u. – arbitrary units; df – degrees of freedom.

In Ukraine, provided that the established hygienic and agrotechnical regulations for the application of the studied products are observed, the risk of their active substances to workers is less than 100% of the permissible level (risk less than 1), which is also confirmed by the indicators obtained in studies conducted in the EU and the USA using various models: for imazamox the risk is 0.8-2.6% of AOEL (2.25 mg/kg bw/day) [15], for imazapyr – 0.06 HQ (hazard quotient at RfD of 2.5 mg/kg bw/day (HQ=1)) [16], for S-metolachlor <100% of AOEL (0.15 mg/kg bw/day) [17], for propisochlor 64% of AOEL (0.025mg/kg bw/day) [18], for tribenuron-methyl <19% of AOEL (0.05 mg/kg bw/day) [19], for terbuthylazine – 16-97% of AOEL (0.0032 mg/kg bw/day) [20], and which statistically does not differ from the results obtained by us using the model adopted in our country [6]: for imazamox the complex risk is 5.99-11.96%, for imazapyr – 0.23-0.43%, for S-metolachlor – 13.06-22.59%, for propisochlor – 12.48-19.55%, for tribenuron-methyl – 6.68-8.08%, for terbuthylazine – 11.85-11.96% of the permissible risk of impact for the applicator and tractor operator, respectively.

CONCLUSIONS

1. It has been established that under real conditions of sunflower crop treatment with the preparations AGAT, GARPUN, KORVUS, and PARUS, when recommended agrotechnical and hygiene regulations for safe use are followed, there is no increase in hygiene standards in the working zone air. It has been demonstrated that the professional risk associated with their use does not exceed the permissible level (<1).

2. Statistical analysis of the obtained results revealed that the values of inhalation, percutaneous, and complex risks during the application of the studied formulations did not significantly differ during various technological operations (for applicators and tractor operators) (p>0.05). The values of the combined complex risk of using the studied preparations did not differ significantly (p>0.05). The proportion of percutaneous risk was significantly higher among applicators compared to the corresponding indicator in tractor operators (p=0.034).

3. Safe usage regulations for the mentioned preparations have been justified. When using AGAT, GARPUN, KORVUS, the workers can enter treated

areas for mechanized work after 3 days and for manual work performing without any specific waiting period. When using PARUS, workers can enter treated areas for mechanized work after 7 days, and there is no waiting period for manual work performing.

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