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PREDICTION OF THE OCCURRENCE OF ACUTE TOXIC EFFECTS DURING SKIN AND INHALATION INFLUENCE OF FUNGICIDES DIFFERENT CLASSES ON AGRICULTURAL WORKERS

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Introduction. The problem of the occupational safety stays relevant. A special issue is given to the effect of dermal chemical protection agents through direct contact. The most common occupational skin diseases associated with the using of pesticides are onycholysis, contact dermatitis, and nail deformation.

The aim of the research is prediction of the occurrence of acute toxic effects during dermal and inhalation exposure of fungicides different classes on agricultural workers.

Materials and methods of the research. Prediction of acute toxic effects was done by using the coefficient of possible inhalation poisoning (CPIP), the coefficient of selective action of the pesticide after inhalation and dermal exposure ($CSA_{ing.}$, $CSA_{d.}$). Statistical analysis of the obtained results was carried out using the MS Excel program (2000) and the license package IBM SPSS Statistics Base v.22.

Results. It has been established that for CPIP all analyzed fungicides of different classes are of low danger (IV class of danger) according to DSanPiN 8.8.1.002-98. The ranking of fungicides according to this criterion shows that the most dangerous are fungicides of anilinopyrimidines class > amides > phenylpyrroles and thiazoles > benzamides and triazoles. A comparative analysis of CSA values for different ways of exposure of the studied active substances showed that it is significantly higher with dermal exposure for almost all analyzed classes of fungicides ($p \leq 0.05$), with the exception of mandipropamide, for which the differences were insignificant ($p > 0.05$). Significantly higher CSA values were obtained in inhalation exposure, compared to CSA values in dermal exposure of the analyzed pesticide formulations ($p \leq 0.05$). The obtained results showed that almost all formulations of fungicides are significantly more dangerous during inhalation way of exposure.

Conclusions. Our findings indicate a significantly higher risk for professional groups when using the analyzed fungicides with inhalation exposure, which should be taken into account when planning work with this group of chemical plant protection products.

Key words: pesticides, risk, prediction occupational skin diseases, poisoning, chemical pollution of working zone

Introduction

The issue of ensuring a safe production environment remains of paramount importance. Within this context, particular attention is directed towards comprehending the impact of chemical protective agents when they come into direct contact with the skin. It is well-established that the consequences of pesticide exposure can have both acute and chronic effects [1, 2]. Among the spectrum of occupational skin diseases attributed to pesticide handling, prevail onycholysis, contact dermatitis, and nail deformations [3].

The aim of the research is to predict the likelihood of acute toxic effects arising from the skin contact and inhalation exposure of agricultural workers to fungicides belonging to distinct classes.

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Materials and methods of the research

The following modern fungicides were studied: Orondis Ultra (mandipropamide, 250 g/l + oxathiapiproline, 30 g/l), Switch (cyprodinil, 375 g/kg + fludioxonil, 250 g/kg), Tsideli Top (difenoconazole, 125 g/kg l + cyflufenamide, 15 g/l), Rias (difenoconazole, 150 g/l + propiconazole, 150 g/l), Monkat (flutolanil, 460 g/l), Bumper (propiconazole, 250 g/l), Kitch (cyprodinil, 375 g/kg, fludioxonil, 250 g/kg), Protect Fungus (difenoconazole, 150 g/l + propiconazole, 150 g/l), Split (difenoconazole, 250 g/l).

The anticipation of acute toxic effects stemming from various fungicide classes on agricultural workers was undertaken following the guidelines provided by SSanRN 8.8.1.002-98 [4] upon the utilization of the Coefficient of Possible Inhalation Poisoning (CPIP) as an indicator for assessment. The following CPIP criteria were employed for the evaluation: a CPIP value of 10 corresponds to an extreme level of danger, classifying the pesticides within the first category; CPIP values ranging between 10 and 2.1 indicate a dangerous level of risk, categorizing the pesticides within the second category; for CPIP values between 2 and 0.5, a moderate level of danger is recognized, placing the pesticides within the third category; CPIP values lower than 0.5 signify a low level of danger, categorizing the pesticides within the fourth category.

The coefficient of selective action of the pesticide after inhalation and dermal exposure ($CSA_{ing.}$, $CSA_{d.}$) were chosen for survey. It was chosen as a criteria for assessing the danger of fungicides during deciding the need for monitoring this pesticides [5]. Assessment criteria CSA: < 1 – the pesticide has an extremely low selectivity of action, 1–99 – low selectivity of action, ≥ 100 – sufficient selectivity of action. The lower the value of CSA, the more dangerous the pesticide can be.

For the investigation, the Coefficient of Selective Action (CSA) following both inhalation ($CSA_{ing.}$) and dermal ($CSA_{d.}$) exposure was selected as a pivotal parameter. This choice was predicated on its relevance as a criterion for evaluating the potential hazard posed by fungicides and, subsequently, for determining the necessity of monitoring these pesticides [5]. The assessment of danger based on CSA adheres to the following guidelines: a CSA value below 1 indicates an extremely low level of selectivity in the pesticide's action; CSA values ranging from 1 to 99 suggest a low degree of selectivity in the pesticide's action; CSA values equal to or exceeding 100 signify a satisfactory level of selectivity in the pesticide's action. The CSA value, when lower, implies a greater potential danger presented by the pesticide.

Results of the research and their discussion

CPIP values of analyzed fungicides of triazoles (difenoconazole, propiconazole), amides (mandipropamide, cyflufenamide), thiazoles (oxathiapiproline), fenipyrroles (fludioxonil), benzamides (flutolanil), anilinopyrimidines (cyprodinil) classes are listed in the Table 1. The calculations showed that the CPIP values of fungicides of the triazole class were $1.68 \cdot 10^{-09}$, amides – $3.06 \cdot 10^{-08} - 1.26 \cdot 10^{-06}$, thiazoles – $5.04 \cdot 10^{-08}$, fenipyrroles – $1.52 \cdot 10^{-08}$, benzamides – $9.08 \cdot 10^{-09}$, anilinopyrimidines – $3.92 \cdot 10^{-05}$. Based on this criterion, all analyzed fungicides belonging to different classes are categorized as having a low level of danger, aligning with the IV class of danger as per SSanRN 8.8.1.002-98 classification.

Ranking of studied fungicides according to this criterion of plants, the most dangerous are the fungicides of class anilinopyrimidines > amides > phenylpyrroles and thiazoles > benzamides and triazoles.

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The values of CSA (Table 1) showed that the values of CSAd. of the triazole class fungicides were (1274.0 ± 169.0) – (2040.68 ± 259.21), amides – (2855.18 ± 1140.13) – (9449.78 ± 806.51), thiazoles – (17646.89 ± 3357.91), fenipyrroles – (2469.16 ± 300.53), benzamides – 3354.80, anilinopyrimidines – (788.89 ± 179.03). All analyzed fungicides demonstrated a satisfactory level of selectivity of action in case of dermal exposure.

During inhalation exposure, the $CSA_{ing.}$ for various fungicide classes exhibited the following ranges: thriazoles (326.0 ± 42.16) – (480.21 ± 57.75), amides (469.49 ± 187.48) – (3598.48 ± 307.12), thiazoles – (2823.50 ± 537.27), fenipyrroles – (513.58 ± 62.51), benzamides – 641.98, anilinopyrimidines – (75.73 ± 17.19). All analyzed fungicides demonstrated a satisfactory level of selectivity of action upon inhalation, with the exception of cyprodinil, a fungicide from the anilinopyrimidine class, which exhibited low selectivity of action.

A comparative analysis of the computed CSA values for various modes of exposure to the studied fungicides unveiled a significant elevation in values with dermal exposure across nearly all analyzed fungicide classes ($p \leq 0.05$), except for mandipropamide, where the observed differences were statistically unreliable ($p > 0.05$).

The outcomes of the analysis regarding the likelihood of acute toxic effects for the formulated preparations of the examined fungicides have been presented in Table 2.

The $CSA_{d.}$ index spans from (137.17 ± 9.69) for Kitch to (81234.57 ± 237.59) for Protect Fungus. Notably, the $CSA_{d.}$ values indicate that all formulations of the tested fungicides exhibit satisfactory selectivity of action.

$CSA_{ing.}$ values spans from (2961,04 ± 248,28) for Switch to (50192,73 ± 13628,41) for Split. The analysis of $CSA_{ing.}$ values has demonstrated the presence of sufficient selectivity of action for all the examined fungicides.

In most cases, $CSA_{ing.}$ values were notably higher than the $CSA_{d.}$ values derived from the analysis of pesticide formulations ($p \leq 0.05$). The outcomes of this analysis indicate that nearly all fungicide formulations pose a significantly greater risk when exposed through inhalation.

Previous investigations conducted by other experts have yielded findings that align with the current study's focus, notably that the CSA values for diverse modes of fungicide exposure, particularly those based on active substances that induce the liver's monooxygenase system, as well as combined fungicides incorporating difenoconazole, consistently exceeded 100. This finding suggests a relative level of safety associated with these fungicides. In contrast, CSA values for avermectins were observed to be up to 99, indicating a lower level of selectivity in their action [6–8]. Similar trends have been documented in parallel investigations on prediction of danger towards workers engaged in the cultivation of various agricultural crops [9, 10].

A comparative analysis of the computed CPIP values from both our own research and relevant literature sources for fungicides belonging to various classes, including amides, anilides, analides, anilinopyrimidines, benzanilides (cyfluphenamide, mandipropamide, phenhexamide, cyprodinil, metalaxyl-M, flutolanil, fluxapiroxad), triazoles and oxazoles (difenoconazole, propiconazole, penconazole, tebuconazole, oxathiapiproline, famoxadone, pacrobutlazol), phenylpyrroles (fludioxonil), was conducted. Remarkably, the results indicated no significant differences ($p > 0.05$) in CPIP values, apart from the CPIP indicator for phenylpyrroles, where a significant distinction emerged ($p = 0.01$ based on the Wilcoxon W-test) (Table 3).

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Table 1

The potential occurrence of acute toxic effects upon contact with active substances of fungicides

Active substances	Formulation	Coefficient of Possible Inhalation Poisoning (CPIP)	Rate of active substances application, kg/ha	Coefficient of selective action $CSA_{ing.}$	Coefficient of selective action $CSA_{d.}$	$t_{ing. – d.}$ (p =)
Difenoconazole	Tsideli Top	$1.68 \bullet 10^{-09}$	0.075	434.57	1654.32	7.45 (< 0.001)
	Tsideli Top		0.08375	389.17	1481.48	
	Tsideli Top		0.05	651.85	2481.48	
	Rias		0.075	434.57	1654.32	
	Rias		0.12	477.37	2057.61	
	Rias		0.135	241.43	919.07	
	Rias		0.15	381.89	1646.09	
	Protect Fungus		0.1125	289.71	1102.88	
	Protect Fungus		0.12	271.60	1033.95	
	Protect Fungus		0.15	217.28	827.16	
	Split		0.1875	173.83	661.73	
	Split		0.225	144.86	551.44	
	Split		0.25	130.37	496.30	
	M ± m		0.13 ± 0.02	326.0 ± 42.16	1274.0 ± 169.0	
Mandipropamide	Orondis Ultra	$3.06 \bullet 10^{-08}$	0.25	205.04	1246.91	2.50 (0.088)
	Orondis Ultra		0.05	1025.19	6234.57	
	Orondis Ultra		0.15	341.73	2078.19	
	Orondis Ultra		0.1675	306.03	1861.07	
	M ± m		0.154 ± 0.040	469.49 ± 187.48	2855.18 ± 1140.13	
Flutolanil	Monkat	$9.08 \bullet 10^{-09}$	0.092	641.98	3354.80	–
Oxathiapiproline	Orondis Ultra	$5.04 \bullet 10^{-08}$	0.015	3292.18	20576.13	5.26 (0.013)
	Orondis Ultra		0.012	4115.23	25720.16	
	Orondis Ultra		0.024	2057.61	12860.08	
	Orondis Ultra		0.027	1828.99	11431.18	
	M ± m		0.020 ± 0.004	2823.50 ± 537.27	17646.89 ± 3357.91	
Cyflufenamide	Tsideli Top	$1.26 \bullet 10^{-06}$	0.01125	4178.88	10973.94	11.7 (0.007)
	Tsideli Top		0.0135	3482.40	9144.95	
	Tsideli Top		0.015	3134.16	8230.45	
	M ± m		0.013 ± 0.001	3598.48 ± 307.12	9449.78 ± 806.51	

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Continuation of the Table 1

Active substances	Formulation	Coefficient of Possible Inhalation Poisoning (CPIP)	Rate of active substances application, kg/ha	Coefficient of selective action $CSA_{ing.}$	Coefficient of selective action $CSA_{d.}$	$t_{ing. - d.}$ (p =)
Propiconazole	Rias	$1.68 \cdot 10^{-09}$	0.15	217.28	827.16	7.74 (< 0.001)
	Rias		0.075	763.79	3292.18	
	Rias		0.09	362.14	1378.60	
	Rias		0.105	545.56	2351.56	
	Bumper		0.2	286.42	1234.57	
	Bumper		0.125	458.27	1975.31	
	Bumper		0.15	381.89	1646.09	
	Protect Fungus		0.105	545.56	2351.56	
	Protect Fungus		0.12	477.37	2057.61	
	Protect Fungus		0.075	763.79	3292.18	
	M ± m		0.120 ± 0.012	480.21 ± 57.75	2040.68 ± 259.21	
Fludioxonil	Switch	$1.52 \cdot 10^{-08}$	0.075	342.39	1646.09	8.22 (< 0.001)
	Switch		0.05	513.58	2469.14	
	Switch		0.0375	684.77	3292.18	
	Kitch		0.05	513.58	2469.14	
	Kitch		0.075	342.39	1646.09	
	Kitch		0.0375	684.77	3292.18	
	M±m		0.050 ± 0.007	513.58 ± 62.51	2469.16 ± 300.53	
Cyprodinil	Switch	$3.92 \cdot 10^{-05}$	0.1125	105.35	1097.39	4.41 (0.005)
	Switch		0.075	158.02	1646.09	
	Switch		0.13125	90.30	940.62	
	Kitch		0.1875	63.21	658.44	
	Kitch		0.28125	42.14	438.96	
	Kitch		0.3	39.51	411.52	
	Kitch		0.375	31.60	329.22	
	M ± m		0.21 ± 0.04	75.73 ± 17.19	788.89 ± 179.03	

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Table 2

The potential occurrence of acute toxic effects upon contact with fungicide formulations

Formulation	Rate of application of formulation, kg(l)/ha	Rate of application of formulation, kg(l)/ha M ± m	Coefficient of selective action $CSA_{ing.}$	Coefficient of selective action $CSA_{ing.}$ M ± m	Coefficient of selective action $CSA_{d.}$	Coefficient of selective action $CSA_{d.}$ M ± m	$t_{ing.-d.}$ (p =)
Orondis Ultra	0.6	0.54 ± 0.06	8773.66	10079.89 ± 1166.86	514.40	590.99 ± 68.41	8.64 (0.003)
	0.67		7857.01		460.66		
	0.4		13160.49		771.60		
	0.5		10528.40		617.28		
Tsideli Top	0.8	0.90 ± 0.06	7765.43	6960.13 ± 449.26	154.32	138.32 ± 8.93	15.50 (0.004)
	0.9		6902.61		137.17		
	1.0		6212.35		123.46		
Switch	0.75	0.85 ± 0.08	3305.35	2961.04 ± 248.28	164.61	147.46 ± 13.36	11.90 (0.006)
	0.8		3098.77		154.32		
	1.0		2479.01		123.46		
Kitch	0.75	0.93 ± 0.06	6584.36	5486.97 ± 387.99	164.61	137.17 ± 9.69	14.10 (< 0.001)
	0.9		5486.97		137.17		
	1.0		4938.27		123.46		
	1.0		4938.27		123.46		
Monkat	0.2	0.2	10622.22	–	1234.57	–	–
Rias	0.5	0.65 ± 0.07	3950.62	3133.45 ± 320.33	246.91	195.84 ± 20.02	9.78 (0.002)
	0.6		3292.18		205.76		
	0.7		2821.87		176.37		
			2469.14		154.32		
Bumper	0.5	0.33 ± 0.09	18686.42	32182.17 ± 8108.09	493.83	850.48 ± 214.27	3.97 (0.057)
	0.3		31144.03		823.05		
	0.2		46716.05		1234.57		

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Continuation of the Table 2

Formulation	Rate of application of formulation, kg(l)/ha	Rate of application of formulation, kg(l)/ha M ± m	Coefficient of selective action $CSA_{ing.}$	Coefficient of selective action $CSA_{ing.}$ M ± m	Coefficient of selective action $CSA_{d.}$	Coefficient of selective action $CSA_{d.}$ M ± m	$t_{ing.-d.}$ (p =)
Protect Fungus	0.15	0.22 ± 0.04	26337.45	19753.09 ± 3801.48	1646.09	1234.57 ± 237.59	5.20 (0.035)
	0.2		19753.09		1234.57		
	0.3		13168.72		823.05		
Split	0.2	0.35 ± 0.09	76380.25	50192.73 ± 13628.41	1234.57	811.29 ± 220.28	3.68 (0.066)
	0.35		43645.86		705.47		
			30552.10		493.83		
M ± m			15060 ± 3244		517.0 ± 85.09		–* (< 0.001)

*Note. *Values were compared using the Wilcoxon T-test.*

Upon conducting a comparative analysis of CSA values during dermal and inhalation exposure, significant differences ($p \leq 0.05$) were evident when various classes of fungicides were employed.

Conclusions

The assessment reveals that, based on the CPIP, all examined fungicides across diverse classes are classified as low in danger, corresponding to the IV class of danger as per SSanRN 8.8.1.002-98. When considering the ranking of fungicides according to this criterion, the following order emerges in terms of decreasing danger: anilinopyrimidines > amides > phenylpyrroles and thiazoles > benzamides and triazoles.

A comparative analysis of CSA values across distinct modes of influence of the studied active substances showed them to be significantly higher with dermal exposure for nearly all the analyzed fungicide classes ($p \leq 0.05$). Notably, this pattern did not apply to mandipropamide, where the observed differences in CSA values were deemed insignificant ($p > 0.05$).

The analysis unveiled significantly higher values of CSA in instances of inhalation exposure, compared to the CSA values observed during dermal exposure of the analyzed pesticide formulations ($p \leq 0.05$). These results indicate that nearly all fungicide formulations manifest significantly higher danger levels when exposed through inhalation pathways.

The investigation established a notably greater level of danger for professional cohorts when employing the analyzed fungicides through inhalation exposure. This finding must be duly considered when working with this particular group of chemical plant protection agents.

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Table 3

A comparative analysis of the potential for acute toxic effects during fungicide application

Classes of pesticides	Sources	Coefficient of Possible Inhalation Poisoning (CPIP)	t_{OR-S} (p =)	Coefficient of selective action $CSA_{ing.}$ M ± m	t_{OR-S} (p =)	Coefficient of selective action $CSA_{d.}$ M ± m	t_{OR-S} (p=)	$t_{ing.-d.}$ (p =)
Amides, anilides, analides, anilinopyrimidine, benzanilides	[8. 9. 10]	$1.7 \cdot 10^{-6} \pm 2.9 \cdot 10^{-5}$ ($9.78 \cdot 10^{-9}$– $1.65 \cdot 10^{-4}$)*	0.8801	121.7 ± 668.0 (31.6–2350.6)	0.7881	664.5 ± 1704.0 (329.2–6172.8)	0.2961	< 0.0011
	Own research	$1.3 \cdot 10^{-6} \pm 6.5 \cdot 10^{-6}$ ($3.06 \cdot 10^{-08}$– $3.92 \cdot 10^{-05}$)		205.0 ± 460.9 (63.2–1025.2)		1646.1 ± 1158.0 (658.4–6234.6)		
Triazoles, oxazoles	[8. 9. 10]	$1.7 \cdot 10^{-9} \pm 3.68 \cdot 10^{-6}$ ($1.66 \cdot 10^{-9}$– $3.1 \cdot 10^{-8}$)	0.7241	490.1 ± 181.6 (250.7–814.8)	0.9541	1718.1 ± 750.9 (954.4–4115.2)	0.8441	< 0.0011
	Own research	$5.04 \cdot 10^{-8} \pm 1.95 \cdot 10^{-7}$ ($1.68 \cdot 10^{-9}$– $1.35 \cdot 10^{-6}$)		434.6 ± 233.2 (289.7–545.6)		1654.3 ± 1515.0 (1234.6–2351.6)		
Phenylpyrroles	[8. 10]	$1.51 \cdot 10^{-8} \pm 7.2 \cdot 10^{-11}$ ($1.5 \cdot 10^{-8}$– $1.52 \cdot 10^{-8}$)	0.0101	308.2 ± 148.7 (102.7–513.6)	0.2571	1481.0 ± 714.7 (493.8–2469.1)	0.2571	0.0021
	Own research	$1.52 \cdot 10^{-8} \pm 2.61 \cdot 10^{-17}$ ($1.52 \cdot 10^{-8}$– $1.53 \cdot 10^{-8}$)		513.6±78.35 (342.4-684.8)		2469.1 ± 376.7 (1646.1–3292.2)		

*Note. Values were compared using the Wilcoxon T-test., *95 % confidence interval.*

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