FORECASTING THE DEVELOPMENT OF ACUTE TOXIC EFFECTS IN PROFESSIONAL CONTINGENTS AFTER COMBINED PESTICIDES APPLICATION FOR AGRICULTURAL CROPS PROTECTION

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Abstract. In the overall structure of occupational diseases the large proportion is acute pesticide poisoning (mainly group cases). In recent decades in the structure of agricultural workers' occupational diseases chemicals poisoning was 14,7–43,5 %.

That is why the purpose of the work was to predict the possibility of acute toxic effects on agricultural workers when working with combined formulations.

Methods. In order to assess the effects of the aforementioned substances on the workers' organism the coefficient of possible inhalation poisoning (CIPP), the coefficient of pesticide effect selectivity at inhalation effect (CPESinhal.) and at dermal application (CPESderm.) were used.

Results. According to the "Hygienic Classification of Pesticides by Degree of Danger", all studied compounds, as well as combined preparations based on them, are pertained to 4th hazard according to this criterion (CIPP<0,5). Calculated CPESinhal. (103,4–4701,2) and CPESderm. (237,4–12345,7) values for all investigated a. i. were more than 100, which indicates a rather high selectivity of their action.

Discussion. Thus, the obtained results allow to predict the possible negative influence of pesticides of different classes on the initial stages of registration tests of pesticide formulations containing studied active substances

Conclusion. The importance of observance of the established regulations for formulations application (norms and rates of application) and the obligatory use of the recommended individual protecting means for the respiratory and skin protection by agricultural workers during the application of studied pesticides are shown.

Keywords: acute poisoning, risks, coefficient of pesticide effect selectivity, dermal and inhalation effects, coefficient of inhalation poisoning possibility.

1. Introduction

According to the Social Insurance Fund of Ukraine economic costs of accidents at work and occupational diseases each year are nearly 1 billion USD [1, 2]. In the overall structure of occupational diseases large proportion are acute pesticide poisoning (mainly group cases) [3, 4]. In recent decades in the structure of agricultural workers' occupational diseases chemicals poisoning was 14,7–43,5 % [4, 5]. These poisonings are common, occur in people of working age and cause prolonged disability that leads to significant social and economic losses [4, 5].

However, today it is impossible to refuse the use of pesticides in agriculture. Their application ensures high biological and economic efficiency of the latter, reduces crop losses [6, 7].

That is why **the** aim of the work was to predict the possibility of acute toxic effects on agricultural workers when working with combined formulations.

2. Methods

The assessment of acute poisoning risk in workers who used combined formulations for crops treatment was carried out taking into account the physical and chemical properties and application rates of active ingredients (a. i.) that are included in their composition: difenoconazole, tebuconazole, propiconazole, paclobutrazole, cyflufenamide, thiamethoxam, azoxystrobin, imidacloprid, fluentuanate, metrubusin, dimetomorph, mancozeb, diquat. In order to assess the effects of the aforementioned substances on the workers' organism the coefficient of possible inhalation poisoning (CIPP), the coefficient of pesticide effect selectivity at inhalation effect (CPESinhal.) and at dermal application (CPESderm.) were used (**Table 1**).

The calculation of the CIPP was carried out according to the equation [8]:

$$CIPP = C_{20}/LC_{50},$$

where C_{20} – concentration of pesticide, which is maximally achievable in air (volatility) at a temperature of 20 °C, mg/m^3; LC_{50} – medium lethal concentration of pesticide in air, mg/m^3.

At the magnitude of KMIO >10 – pesticides are extremely dangerous (1st class), 10–2,1 – dangerous (2nd class), 2–0,5 – moderately dangerous (3rd class), <0,5 – low dangerous (4 class) [9].

Determination of CPES in case of possibility of acute effect with a. i. inhalation and dermal exposure were carried out according to the next equations [8]:

$$CPESinhal. = (LC_{50} \times 0{,}16)/(H \times 16{,}2),$$

where LC_{50} – the medium lethal concentration in air for laboratory rats, mg/m^3; 0,16 – coefficient of conversion of concentration in a dose; H – a. i. application rate, kg/ha; 16.2 – coefficient that takes into account the weight and area of the body of laboratory rats, the dose and application rate.

$$CPESderm. = (LD_{50}d.)/(H \times 16{,}2),$$

where LD_{50}d. – medium lethal dose when applying a. i. on the skin of laboratory rats, mg/kg; H – application rate of a. i., kg/ha; 16.2 – coefficient that takes into account the weight and area of the body of laboratory rats, the dose and application rate.

In assessing the indices, it was believed that at the value of the CPES<1 pesticide has an extremely low selectivity of action, with a CPES value from 1 to 99 – low selectivity of action, with CPES >100 – sufficient selectivity of action.

3. Results

By the magnitude of saturated vapor pressure all studied a. i. are non-volatile (pressure $<1\times\times10^{-5}$ Hg mm). Tebuconazole, propiconazole and cyflufenamide, which are moderately volatile, and volatile flufenacet, metribusin, dimetomorph, mancozeb, diquat are only exceptions (**Table 1**).

The CIPP values of studied fungicides difenoconazole, tebuconazole, cyflufenamide, propiconazole, fludioxonil, pacloburatrazole, thiamethoxam, azoxystrobin, dimetomorph and mancozebe are $1{,}7'10^{-9}$, $3{,}1'10^{-8}$, $1{,}2'10^{-6}$, $1{,}3'10^{-6}$, $1{,}5'10^{-8}$, $7{,}0'10^{-9}$, $2{,}1'10^{-10}$, $2{,}6'10^{-9}$, respectively, herbicides flufenacet, metrubusin, diquat – $3{,}6\times10^{-3}$, $1{,}7\times10^{-2}$, $7{,}7\times10^{-5}$, respectively, insecticide imidacloprid – $7{,}6\times10^{-9}$, indicating a low probability of acute inhalation poisoning with the use of formulations on their basis, including combined. According to the "Hygienic Classification of Pesticides by Degree of Danger" [9], all studied a. i., as well as combined preparations based on them, are pertained to 4th hazard according to this criterion (CIPP <0,5).

Table 1

Assessment of the risk of acute toxic effects development in the application of investigated active substances

Pesticide class	Active ingredient	Formulation	Vapour pressure, Hg mm	Mol. mass, g/mol	Volatility, mg/m^3	CIPP	A.i. application rate, kg/ha	$CPES_{inhal..}$	$CPES_{derm}$
Triazole	difenoconazole	Skor	$2,5\times 10^{-10}$	406,3	$5,5\times10^{-6}$	$1,7\times10^{-9}$	0,13	250,7	954,4
		Amistar Gold					0,13	250,7	954,4
		Magnello					0,25	130,4	496,3
		Rias					0,12	271,6	1033,9
		Seles Top					0,03*	1086,4	4135,8
		Dynali					0,04	814,8	3101,9
		Cideli Top					0,09	362,1	1378,6
		Setar					0,13	103,4	393,7
	tebuconazole	Magnello	$9,8\times10^{-9}$	307,8	$1,6\times10^{-4}$	$3,1\times10^{-8}$	0,1	502,7	1234,6
	propiconazole	Rias	$4,2\times10^{-7}$	342,2	$7,7\times10^{-3}$	$1,3\times10^{-6}$	0,12	477,4	2057,6
	paclobutrazole	Setar	$1,4\times10^{-8}$	293,8	$2,2\times10^{-5}$	$7,0\times10^{-9}$	0,06	515,2	4115,2
Amide	cyflufenamide	Dynali	$2,7\times10^{-7}$	412,4	$5,9\times10^{-3}$	$1,2\times10^{-6}$	0,02	2350,6	6172,8
		Cideli Top					0,01	4701,2	12345,7
Neonicotinoid д	thiamethixam	Seles Top	$5,0\times10^{-11}$	291,7	$7,7\times10^{-7}$	$2,1\times10^{-10}$	0,52*	70,7	237,4
Strobileurine	azoxystrobine	Amistar Gold	$8,3\times10^{-13}$	403,4	$1,8\times10^{-5}$	$2,6\times10^{-9}$	0,13	52,4	949,7
Oxyacetamide	flufenacet	Artist	$6,75\times10^{-4}$	363,3	13,4	$3,6\times10^{-3}$	0,6	61,6	205,8
Triazinone	metribuzine	Artist	$9,1\times10^{-4}$	214,3	10,9	$1,7\times10^{-2}$	0,44	14,7	282,1
Neonicotinoid	imidaclopride	Colt Power	$3,0\times10^{-9}$	255,7	$4,2\times10^{-5}$	$7,6\times10^{-9}$	0,035	1552,02	3527,3
Morpholine	dimethomorph	Filder	$7,39\times10^{-6}$	387,9	$1,6\times10^{-1}$	$3,7\times10^{-5}$	0,18	233,9	1724,1
Carbamate	mancozeb	Filder	$9,75\times10^{-6}$	271,2	$1,4\times10^{-1}$	$3,0\times10^{-5}$	1,2	39,2	102,9
Bipyridylium	diquat	Reglon Forte	$7,5\times10^{-6}$	184,2	$7,5\times10^{-2}$	$7,7\times10^{-5}$	0,3	199,6	411,5

Notes*: CIPP – coefficient of inhalation poisoning possibility; CPES – coefficient of pesticide effect selectivity*

Calculated CPESinhal. (103,4–4701,2) and CPESderm. (237,4–12345,7) values for all investigated a. i. were more than 100, which indicates a rather high selectivity of their action (**Table 1**). Thiamethoxam (Celest Top), azoxystrobin (Amistar Gold), flufenacet and metrubuzin (Artist) and mancozeb (Filder), CPESinhal. of which there were respectively 70,7; 52,4; 61,6; 14,7 and 39,2, which indicates a relatively low selectivity of their action, were exceptions. The obtained results indicate a high probability of occurrence of acute toxic effects when thiamethoxam, azoxystrobin, flufenacet, metrubuzine and mancozeb enter in the body of workers by inhalation. When the same five substances are introduced through the skin, as well as the remaining substances under study, both through the skin and the respiratory tract, the probability of acute toxic effects in the agricultural workers is low.

4. Discussion

The results obtained by us correlate with the data of studies conducted in the soil-climatic conditions of Ukraine. Namely that when using pesticides of studied classes of triazoles, strobilurines, ethylene bis-dithiocarbamates, cyanopyrrols, anilides, anilinopyrimidines for the protection of crops with maximum application rates, the CIPP magnitude did not exceed 8,9×10-6. CPESderm. of fungicides of all studied classes, CPESinhal. of the anilides, cyanopyrroles class compounds are >100, indicating a low probability of the danger of toxic effects development. Triazoles, strobilurines, ethylene-bis-dithiocarbamates, anilinopyrimidines CPES values in most of cases are in the range of 1–99, which indicates a relatively high probability of acute toxic effects when it enters the respiratory system [10].

Thus, the obtained results allow to predict the possible negative influence of pesticides of different classes on the initial stages of registration tests of pesticide formulations containing studied active substances.

Conclusions:

1. It was established that the value of the coefficient of inhalation poisoning possibility <0,5 for all active substances, indicating a low probability of acute poisoning after application of combined formulations on their basis. According to this criterion, all investigated compounds are pertained to 4th class of hazard according to State Standards 8.8.1.002-98.

2. Relative safety in the percutaneous and inhalational way of the agricultural workers' exposure has been proved, for which the CPESinhal. and CPESderm. >100. Exceptions are thiamethoxam, azoxystrobin, flufenacet, metrubuzin and mancozeb CPESinhal. which values are in the range of 1–99, and CPESderm. >100, indicating a relatively high probability of acute toxic effects in contact with the respiratory system and their low probability after getting into the skin.

3. The importance of observance of the established regulations for formulations application (norms and rates of application) and the obligatory use of the recommended individual protecting means for the respiratory and skin protection by agricultural workers during the application of studied pesticides are shown.

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