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HYGIENIC ASSESSMENT OF OCCUPATIONAL RISK WHEN USING PESTICIDAL FORMULATIONS BASED ON SPIROMESIFEN AND ABAMECTIN FOR AGRICULTURAL WORKERS

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Introduction. Pesticide load is a potential hazard not only for the environment, but also for the people who work with chemical plant protection products. Therefore, the maximum observance of all hygienic requirements and regulations for the use of formulations is very important for the health of workers.

The aim of the study is a hygienic assessment of working conditions and potential occupational risk of hazardous effects of spiromesifen and abamectin (active ingredients of Oberon Rapid 240 SC, KS) when applied to crops.

Materials and methods of research. We carried out the field experiments to study the working conditions of workers with ventilatory treatment of apple trees with the Oberon Rapid 240 SC formulation. The method of gas-liquid, high-performance liquid chromatography and the vapor-phase gas chromatography were used to determine the contents of active ingredients in the air of the working zone, atmospheric air, washes from open surfaces of the skin and rubber gloves, stripes on overalls. The potential risk of a possible dangerous effect of spiromesifen and abamectin on workers with complex intake through the respiratory tract and skin was assessed in accordance with the Guidelines «Studying, assessing and decreasing the risk...» (Approved by MH of Ukraine No. 324, 13.05.2009).

Results. The values of occupational risk for various routes of exposure to spiromesifen and abamectin in a tanker and a tractor driver were calculated, taking into account the content of substances in the air of the working zone, flushes from open skin areas and stripes on overalls do not exceed 1 (permissible risk ≤ 1). The combined risk of harmful effects on workers with a complex intake of spiromesifen and abamectin was calculated by simple summation of the complex risk values. The resulting risk for the tanker was $7.8 \cdot 10^{-4}$ c. u., for a tractor driver – $11.1 \cdot 10^{-4}$ c. u., that is, does not exceed 1 and is an acceptable value. It has been proven that in the formation of a professional combined risk, the leading role belongs to the inhalation (96 %). For the workers the re-enter intervals are as follows: 3 days for mechanized work and 7 days for manual work. We recommend monitoring the application of the formulation using spiromesifen.

Conclusion. It has been shown that the application of the Oberon Rapid 240 SC, which combines two active ingredients – spiromesifen and abamectin, when using traditional technical means and observing the established agro-technical and hygienic regulations, does not pose a danger to workers.

Key words: spiromesifen, hygienic assessment, working conditions, professional risk

Introduction

The uncontrolled use of plant protection chemicals is most dangerous for the environment and the people [1]. This problem is particularly acute among the professionals and it is for their protection that hygienic regulations and conditions for the safe use of pesticide preparations should be developed [2].

Farmers and agriculture, at the current rate of crop chemization, need more effective and less toxic formulations [1, 2]. Compounds with systemic insecticidal action have proven to be very effective against insect pests, which reduces the pesticide consumption by hundreds of times [3]. Spiromesifen, representative of class of derivatives of tetramic and tetronic acids, one of active substances of Oberon Rapid 240 SC, KS, has exactly such property. The second active ingredient of the insecticide, abamectin (class of avermectins), is a neurotoxicant for the target insects [3].

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Risk assessment of the pesticide under study will address worker safety issues during its use.

The aim of the study is the hygienic assessment of working conditions and potential occupational risk of dangerous effects of spiromesifen and abamectin (active substances Oberon Rapid 240 SC, KS) when they are used on agricultural crops.

In order to achieve this goal, the following tasks need to be solved:

- To study working conditions during application of the preparation Oberon Rapid 240 SC, KS by ventilation method on apple-trees at maximum rates of consumption;
- To determine the exposure and justify the permissible inhalation and percutaneous doses of spiromesifen and abamectin;
- To establish the risk of inhalation, percutaneous and combined exposure to the active substances under investigation as well as the combined exposure for occupational contingents.

Materials and methods of research

In situ trials of Oberon Rapid 240 SC, CS on apple-trees were carried out according to [4]. Apple trees were treated in Kyiv region, Skvirsk district, v. Pustovarivka on the base of LLC Agrofirma «KOLOS» with the rate of 0.8 g/ha (spiromesifen – 228.6 g/l, abamectin – 11.4 g/l).

Meteorological conditions during the work are given in Table 1.

The preparation was applied in orchards using OPV-2000 sprayer aggregated with MTZ-82 tractor. Preparation of the working solution was carried out at the treatment area. Duration of working solution preparation – 10 min, duration of treatment – 20 min. Working liquid consumption – 1000 l/ha and area of the treated area – 2 ha.

When filling the sprayer and spraying, the filler and tractor driver were involved, who had a permit to work with pesticides and agrochemicals. For personal protection gloves and respirators were used (when filling), overalls made of synthetic fabric and boots were used.

Working conditions were evaluated based on the results of determination of residual amounts of spiromezifen and abamectin (in the air of the working area, in wipes from exposed skin areas and under workwear, in patches on workwear) using gas-liquid, high-performance liquid chromatography and vapor phase method.

At each step of the process 3 samples were taken in parallel at one point. If the content of the active ingredient in the individual samples or wipes from exposed skin areas and patches on workwear was below the limit of quantification (MCV), 1/2 of the limit of quantification of the method was taken into account.

The MAC of the active substances is given in Table 2.

A large number of models have been used worldwide to assess the risk of potential occupational exposure to pesticides: the «German» model (1992), the «English» model (1990), the «Danish» model (1992), the «North American» model (1992) and the «Russian» model (1992) [2, 5, 6].

In Ukraine, the assessment is performed using the model developed by the Kundiiev Institute of Occupational Health of the National Academy of Medical Sciences of Ukraine, which includes the

Table 1

Meteorological conditions during the work

Date of work	Air temperature at the time of processing, °C	Atmospheric pressure, mm Hg	Relative humidity, %	Wind speed, m/s
29.07.2016	24	750	65	1,0

Note. The results of own measurements at the place of research.

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Table 2

Limits of quantification (LOQ) of spiromesiphene and abamectin in air, skin washings and patches and their hygienic standards

Object	LOQ (No. of methodical instructions)	
	spiromesiphene	abamectin
Atmospheric air, mg/m^3	0.0003/0.002 (No. 1559–2018)	0.00016/0.0002 (No. 1106–2011)
Air of working zone surface, mg/m^3	0.003/0.8 (No. 1559–2018)	0.01/0.04 (No. 1106–2011)
Soil, mg/kg	0.007/0.4 (No. 1563–2018)	0.01/0.3 (No. 1108–2011)
Washings, patches, mg	0.001	0.00002

determination of exposure inhalation doses (D_{ing}) and percutaneous doses (D_{perc}) of active substances, justification of the allowable inhalation doses (DD_{ing}) and percutaneous doses (DD_{perc}) and their comparison in accordance with [5]. During a work shift, the D_{ing} and D_{perc} should not exceed the DD_{ing} and DD_{perc} doses, respectively. That is the ratio of exposure dose to permissible dose (hazard coefficient) shall not exceed 1.0. At the same time the sum of the ratio of exposure and permissible doses for different exposure pathways (hazard index) shall also not exceed 1.0.

Ding was determined taking into account pesticide concentration in the air of working area, standardized human respiratory volume, duration of individual production operation and normalized number of cycles, and D_{perc} was calculated by determining the total actual skin contamination levels after completion of production operation, knowing the normalized number of cycles per work shift and dividing it by the average mass of an adult (70 kg).

To calculate DD_{ing}, the hygienic standard in working area air, standardized human respiratory volume, working shift duration and their product of the average adult body weight were used. The permissible percutaneous dose of DD_{perc} was calculated by the ratio of the product of permissible daily dose (PDD) of the substance for a human and the conversion factor of PDD to non-active oral dose at multiple administration taking into account the hazard class at skin application to the dermal absorption factor.

The combined risk (CR) was determined by simple summation of the risk values for the simultaneous action of spiromesifen and abamectin at complex administration according to the formula:

$$CR = \sum \left(\frac{D_{ing}}{DD_{ing}}\right)_{1,2...n} + \sum \left(\frac{D_{perc}}{DD_{perc}}\right)_{1,2...n},$$

where 1, 2...n are the active substances under study.

Research results and their discussion

The working conditions of a refueller and a tractor driver during the application of Oberon Rapid 240 SC, CS have been studied. It was found that before work, during the operation and after the process, no changes in blood pressure, complaints of general worsening of health, signs of damage to exposed skin and mucous membranes of the workers were observed.

Air sampling during production operations, possible wear of the drug and over the treated area was performed according to [7]. The results of spiromesifen and abamectin determination in the air are presented in Table 3.

Based on the results presented in Table 3, we can conclude that preparation of solutions, filling up of sprayers and treatment of apple-trees with Oberon Rapid 240 SC, CS were not accompanied by chemical compounds in the air of the tanker and tractor driver's breathing zone. Nor were they detected in the air of possible insecticide wear at a distance of 300 m from the edge of the field and in the air above

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Table 3

Content of spiromesiphene and abamectin in the air, in washings from the surface of the skin and from the patches of overalls of workers

Object of research	Content	
	spirimesiphene	abamectin
Washings from the surface, mg on the entire surface:		
Refueller:		
– face and neck	< 0.001*	< 0.00002*
– gloves	0.003	0.0004
– hands	< 0.001*	< 0.00002*
Tractor driver:		
– face and neck	< 0.001*	< 0.00002*
– hands	< 0.001*	< 0.00002*
Patches on overalls in the region, mg/dm^2 of the surface:		
Refueller:		
Upper arm:		
– forearms, chest	0.002	< 0.00002*
– back, thighs	< 0.001*	< 0.00002*
Tractor driver:		
– forearms, chest	< 0.001*	< 0.00002*
– back, thighs	< 0.001*	< 0.00002*
Air of the refueler breathing zone (tank neck), mg/m^3, mg/kg	n/a	< 0.01**
Air of the tractor driver's breathing zone (tractor cab), mg/m^3, mg/kg	n/a	< 0.01**
The air of the work area above the site (center) in:		
– an hour		
– 3 hours	n/a	< 0.01**
– 7 days	n/a	< 0.01*
Air at a distance of 500 m from the edge of the site (upwind side) in:		
– an hour	n/a	< 0.00016**
– 3 hours	n/a	< 0.00016**
Soil, mg/kg:		
– 3 days	< 0.00016	0.16 ± 0.02
– 7 days	< 0.01	0.18 ± 0.02

*Note. *Below the limit of detection in the sample (washings, patches): abamectin – 0.00002 mg, spiromesiphene – 0.001 mg;*
***below the limit of quantitative determination of abamectin: in the air of the working area – 0.01 mg/m^3, atmospheric air – 0.00016 mg/m^3, soil – 0.01 mg/kg;*
n/a – not detected, at the detection limit of spiromesifen:
in the air of the working area – 0.003 mg/m^3; atmospheric air – 0.0003 mg/m^3, soil – 0.007 mg/kg.

the treated area, because in all the samples taken, as well as in the summation of three parallel samples, the content of the active substances under investigation was less than the MCV (Table 3).

The content of spiromesifen and abamectin in wipes from exposed skin surfaces, personal protective equipment and patches from protective clothing of workers after production operations is shown in Table 3.

As it can be seen from the data in Table 3, almost no active substances were detected in the samples from gas station operator and tractor driver, as they were below the limit of quantitative determination of the method. This indicates that the use of personal

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protective equipment and protective clothing reliably protects workers from exposure to the drug.

However, spiromesifen at 0.003 mg and abamectin at 0.0004 mg were detected on the gas station attendant's gloves, and spiromesifen at 0.002 mg on the patches. Therefore, a calculation was made of the complex exposure of these substances to the human body.

Calculation of complex risk for workers taking into account the results of field studies was carried out in accordance with [5].

Results of exposure and permissible doses determination, as well as risk values (hazard coefficient, hazard index, combined risk) are given in Table 4.

As shown in Table 4, the risk values for workers exposed to spiromesifen during apple tree treatment for inhalation ingestion are $0.5 \cdot 10^{-4}$ c. u. for the tanker and $0.8 \cdot 10^{-4}$ c. u. for the tractor driver. The risk values of abamectin for the refueller are $5.0 \cdot 10^{-4}$ c. u. and for the tractor driver, $10.0 \cdot 10^{-4}$ c. u. For percutaneous ingestion, the risk values for the refueller and the tractor driver are – $1.5 \cdot 10^{-4}$ c. u. and $0.25 \cdot 10^{-4}$ c. u., respectively, and abamectin $0.8 \cdot 10^{-4}$ c. u. and $0.04 \cdot 10^{-4}$ c. u., respectively.

Thus, the exposure dose of the active substances investigated by inhalation to the tractor driver is by 2 orders of magnitude higher than the exposure dose of the refueller, while the percutaneous dose of the refueller is, on the contrary, 6 orders of magnitude higher than that of the tractor driver. The permissible doses of spiromesifen and abamectin for percutaneous ingestion in both workers are higher than the inhalation dose by 1 order of magnitude.

The hazard ratio for treatment of horticultural crops with Oberon Rapid 240 SC, KS ranged from $0.5 \cdot 10^{-4}$ to $10.0 \cdot 10^{-4}$ c. u. in the case of inhalation exposure and was tens of orders of magnitude higher than percutaneous exposure, which was $0.04 \cdot 10^{-4}$ to $1.5 \cdot 10^{-4}$ c. u. (Table 4). The

Table 4

Values of occupational hazards in case of complex and combined intake of active substances of Oberon Rapid 240 SC, KS

Personnel	Active substance	Exposure dose, mg/kg, $\cdot 10^{-4}$		Acceptable dose, mg/kg, $\cdot 10^{-4}$		Hazard coefficient, $\cdot 10^{-4}$		Hazard index, $\cdot 10^{-4}$	Combined hasard, $\cdot 10^{-4}$
		inhalational	percutane	inhalational	percutane	inhalational	percutane		
Spiromesiphene	Спіромезіфен	0.06	0.6	0.12	0.4	0.5	1.5	2.0	7.8
	Abamectin	0.2	0.06	0.04	0.08	5.0	0.8	5.8	
Spiromesiphene	Спіромезіфен	0.1	0.1	0.12	0.4	0.8	0.25	1.05	11.1
	Abamectin	0.4	0.003	0.04	0.08	10.0	0.04	10.04	

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inhalation hazard ratio for abamectin was 11.5 times higher than for spiromesifen, and for percutaneous ingestion it was 2 times higher for spiromesifen than for abamectin. For the refueller, the hazard rate for percutaneous exposure was 7 times higher than for the tractor driver, due to greater exposure to the drug when refuelling the sprayer tank. In the case of inhalation exposure, on the contrary, the tractor driver had almost 2 times the danger indicator compared to the filler, which can be explained by the longer duration of the operation.

As Oberon Rapid 240 SC insecticide is a combined preparation, the hazard index and the total combined risk of exposure to its active substances were calculated. In this case, it was considered possible to identify the negative effects of the chemical compounds under study. It was found that the share of inhalation hazard index in the hazard index of spiromesifen and abamectin is 96 %. Having calculated the hazard indices of complex exposure to the two studied active substances of the preparation (Table 4) constituting $2.0–5.8 \cdot 10^{-4}$ and $1.05–10.04 \cdot 10^{-4}$ c. u. for a refuelling agent, we can conclude that it is less than unity.

The combined risk for the refueller was $7.8 \cdot 10^{-4}$ c. u. and for the tractor driver was $11.1 \cdot 10^{-4}$ c. u., which is also less than unity and is acceptable with the combined effect of the drug, which means that no potential adverse effects of the drug are expected for both workers.

In order to justify the timing of workers leaving the treated areas and to assess the degree of danger due to windward wear for those working on adjacent plots, the spiromesifen and abamectin content was determined in the air above the treated area and in the zone of possible wear at a distance of 500 m from the border 1 and 3 hours after treatment (Table 3). Soil, air above the treated area and the 300 m zone of possible wear (sanitary protection zone) were sampled at 3 and 7 days after the operation in order to determine the dynamics of pollution reduction.

It was found that both on the day of treatment, and all subsequent periods of observation residual amounts of the active substances in the air over the treated area and in the air at a distance of 300 and 500 m from the border of the treated area to the leeward side did not exceed the MAC and TOC in the working air. The air quality in the treated area (spiromesifen 0.003/0.08 mg/m^3, abamectin 0.01/0.04 mg/m^3) and ambient air (spiromesifen 0.0003/0.002 mg/m^3, abamectin 0.00016/0.0002 mg/m^3) (Table 2).

Examination of soil samples showed that on days 3 and 7 the content of active substances of the drug did not exceed the established hygienic norms in soil: MPC of spiromesifen – 0.4 mg/kg, that of abamectin – 0.3 mg/kg (Table 2).

Calculation data of determination of residual quantities of the studied substances in samples in air and soil (lower MCV/ASLI/APC) indicate the absence of hazardous effects of the preparation on environmental objects.

The results of the study of working conditions during Oberon Rapid 240 SC, CS treatments with a fan sprayer showed that when using the pesticide at the maximum consumption rate of 0.8 l/ha no exceeding of hygienic standards in the working area air, the atmospheric air near the treatment. soil and no deterioration of working conditions were observed. It was found that already 3 days after treatment with the pesticide the production environment of the treated areas was relatively safe.

Residues of abamectin and spiromesifen in the breathing zone air of the refueller and tractor driver at day 3 and 7 of the study were undetectable or below the MCV. Similar data were obtained in air samples in the area of possible wear and tear. Spiromesifen was found in wipes from forearm and chest patches at 0.02 mg (Table 3), and two active substances were found in wipes from gloves at

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0.005 mg and 0.0004 mg respectively. However, no worsening of the worker's condition was recorded, so this effect was considered non-toxic.

Thus, the above mentioned allowed us to scientifically substantiate the terms of workers' release to the areas treated with Oberon Rapid 240 SC, CS when treating apple-trees: for mechanized works – 3 days, for manual works – 7 days.

From our calculations, given in Table 4, the hazard index of abamectin for the filler is almost 3 times higher than the hazard index of spiromesifen, and for the tractor driver it is almost 10 times higher. For the inhalation hazard index value, abamectin is 11 times higher than spiromesifen. According to the studies of the residue content of the compounds described above, we can conclude that abamectin is more persistent and more toxic than spiromesifen. Therefore, it is recommended to monitor the use of the drug for abamectin.

Conclusions

1. It was found that under actual conditions of treatment of apple trees with the insecticide Oberon Rapid 240 SC, CS by fan sprayer (the rate of consumption is 0.8 kg/ha, twice), there is no exceeding of hygienic standards in the air of the working area and the atmospheric area. and there is no violation of hygiene requirements in terms of occupational safety.
2. The calculated values of combined risk at application of Oberon Rapid 240 SC, CS have shown that at inhalation of active substances – spiromesifen and abamectin, the risk is higher than at percutaneous exposure and is acceptable (not exceeding 1).
3. The terms of safe exit of workers to the treated areas when using the preparation Oberon Rapid 240 SC, KS: 3 days for mechanized works and 7 days for manual works.

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Conflict of interests. The authors declare the absence of potential and obvious conflict of interests related to the manuscript.

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