INTRODUCTION

According to the International Labor Organization [1], agriculture is among the most dangerous to life and health of workers in both industrialized and developing countries. Agriculture employs almost half of the world’s workforce (1.3 billion people), killing up to 170,000 agricultural workers each year as a result of accidents, injuries related to agricultural machinery, poisoning by pesticides and other chemicals [2].

Improving chemical plant protection products (ChPPPs), applied technologies and the integration of chemical, physical and biological knowledge will truly optimize the use of pesticides without compromising the quality and efficiency of agriculture or consumer and environmental protection [3].

The Directive [4], which regulates the actions of citizens to ensure the sustainable and safe pesticides application, amended the safety requirements for pesticide application machines. Particular attention is paid to assessing the risk of using pesticide application machines, ensuring maximum deposition of pesticides on target sites and minimizing losses in non-target areas, which will ensure a high level of protection of human health and safety and the environment.

The sprayer (nozzle) is a key element of the sprayer and the efficiency of processing, economic, operational, hygienic and ecological indicators depend on it. Properly selected nozzles and conditions for pesticide application ensure efficient distribution of the working solution on the target surfaces [5], which reduces the risk of impact on the ecosystem and workers involved in the treatments.

THE AIM

Therefore, the aim of our work was a comparative hygienic assessment of working conditions and occupational risk when applying the fungicide Amistar Extra 280 SC using slotted and injector sprayers.
MATERIALS AND METHODS

Field studies were conducted in 2020 on the basis of Bila Tserkva research station LLC “Syngenta” in the Kiev region using the Amistar Extra 280, SC (80 g/l of cyproconazole and 200 g/l of azoxystrobin) in the maximum application rate of the formulation (0.75 l/ha), working solution – 250 l/ha on soybean crops. When applying the formulation certified equipment was used (trailed boom sprayer AMAZON 1201 UF (1200l), which was combined with a tractor MTZ 82.1 Belarus). Super Poly 110-04 (variant №1) and Guardian Air GA110-04 (variant № 2) sprays were selected for comparative studies. The first of them is a universal slotted sprayer of a wide range, which performs disintegration of the working solution; the second is an air-injector spray, which due to its structure performs air ejection, mixing with liquid and spraying drops with air inclusions.

The refueler carried out preparation of the formulations’ working solution, the duration of the operation was 7-10 minutes. The soybean crops were processed by a tractor driver for 20 minutes. The refueler and the tractor driver were dressed in special protective clothing during the production operations: overalls made of synthetic fabric and boots. Rubber gloves and respirators were used as personal protective equipment.

Air sampling was performed using a portable aspirator “Typhoon”. Air samples were taken on a paper filter “blue tape” and silica gel. When performing each production operation at three parallel points, 3 samples were taken sequentially. Cards, made of water-sensitive paper TeeJet 20301-1N (76 mm×26 mm), were installed at a height of 0.5 m on an artificial support for visual assessment of the presence and density of working solution drops in a possible wear zone (10 m on the leeward side of the field). Evaluation of the result was performed by counting through a magnifying glass the number of drops on the cards that were used during the slotted and injection application of the pesticide. In each variant of the field study, 10 water-sensitive cards with their obligatory numbering were used.

Studies of the pesticides content on the skin surface of the workers were performed after the operation with degreased and soaked in ethyl alcohol diluted in water in a ratio of 1: 1, gauze napkins and stripes (3-layer stripes: outer layer – cotton fabric, middle layer – medical gauze, internal – the filter “blue tape”) on overalls.

Sampling and quantification of the active substances content in the air of the working area, atmospheric air, in washes from exposed skin and gloves, stripes on overalls were performed by high performance liquid and gas-liquid chromatography. Methods, limits of quantitative determination and hygienic standards of the investigated active substances are given in Table I.

Occupational risk assessment was performed in accordance with the guidelines [9]. Because Amistar Extra 280, SC is a combined pesticide, the simultaneous action of two active substances is possible. Therefore, to assess, we calculated the magnitude of occupational risk in the combined exposure of both active substances in one formulation. The combined risk (CR) was determined by simply summing the risk values of several active substances in a complex intake:

\[ CR = \sum \left( \frac{D_{\text{ing}}}{PD_{\text{ing}}} \right)_{1,2...n} + \sum \left( \frac{D_{\text{derm}}}{PD_{\text{derm}}} \right)_{1,2...n} \]

where CR – combined risk;
1, 2, ..., n – studied active substances;
D_{\text{ing}} – a dose of pesticide that enters the worker’s body by inhalation;
D_{\text{derm}} – the dose of pesticide that enters the worker’s body through the skin;
PD_{\text{ing}} – permissible inhalation dose for professional contingents;
PD_{\text{derm}} – permissible percutaneous dose for professional contingents.

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

RESULTS

As a result of field studies of working conditions during pesticide application operations, it was found that the concentration of azoxystrobin and cyproconazole in the air of the refueler’s working zone and the zone of possible wear in all variants of experiments was below the limit of quantitative determination of the method (Table I).

When using the slotted sprayer Super Poly 110-04 (variant №1) in the air of the tractor driver’s working area the content of azoxystrobin was 0.0015±0.0001 mg/m³, cyproconazole – 0.085±0.002 mg/m³. We also analyzed the

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Current norms, LQD</th>
<th>Azoxystrobin</th>
<th>Cyproconazole</th>
</tr>
</thead>
<tbody>
<tr>
<td>The air of the working zone, mg/m³</td>
<td>TSEL 1.0</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>LQD</td>
<td>0.001 (HPLC)</td>
<td>0.05 (GC)</td>
<td></td>
</tr>
<tr>
<td>Atmospheric air, mg/m³</td>
<td>TSEL 0.01</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>LQD</td>
<td>0.001 (HPLC)</td>
<td>0.008 (GC)</td>
<td></td>
</tr>
<tr>
<td>Washes, stripes, mg</td>
<td>LQD 0.002 (HPLC)</td>
<td>0.002 (GC)</td>
<td></td>
</tr>
</tbody>
</table>

content of active substances of the Amistar Extra 280, SC formulation at a distance of 10 m from the edge of the field on the leeward side. The concentration of azoxystrobin in the wear zone when applying the formulation using Super Poly 110-04 was 0.003±0.001 mg/m³, cyproconazole – 0.11±0.02 mg/m³. In the air of the treatment zone (above the field) after 1 hour, 3 days, 7 days and the zone of possible wear at a distance of 100 m from the edge of the site after 1 hour, 3 days, 7 days the concentrations of active substances was below the limit of quantification in atmospheric air.

When applying the pesticide using the injector sprayer Guardian Air GA110-04 (variant №2) in the air of the tractor driver working area the concentration of studied active substances was below the limit of quantification of the method (Table II). In the air of the treatment zone, zones of possible wear (10 and 100 m) in different time intervals the concentration of active substances was below the limit of quantification in atmospheric air.

An analysis of the content of active substances in washes from exposed areas of skin and stripes on staff overalls was performed. It was found that the level of contamination of open (face, neck) and closed areas of the skin of the refueler and tractor driver was below the limit of quantification of the relevant methods. In strips on workers’ overalls, the concentrations of active substances were also below the limit of determination of the method.

The obtained factual data on the assessment of working conditions using the injector sprayer Guardian Air GA110-04 and slotted one Super Poly 110-04 allowed us to calculate the occupational risk of complex intake through the skin and respiratory tract, as well as the combined intake of several active substances in one formulation. (Table III).

Analysis of the data of occupational risk calculations for complex and combined exposure to pesticides showed that the difference in the risks for refuelers of the sprayer tanks in variants №1 and №2 of field studies is not significant according to Student’s criterion (p> 0.05). This is completely comparable to the expected result, as the technologies for preparing the working solution and filling the sprayer tank were identical. The proportion of percutaneous and inhalation risks in azoxystrobin refuelers was 77.4 and 22.6 %, respectively. For cyproconazole, the percutaneous and inhalation risks were 13.4 and 86.6 %, respectively, and the combined risk was 0.04.

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**Table II.** The content of active ingredients of the Amistar Extra 280, SC formulation in air samples using different spraying technologies, mg/m³

<table>
<thead>
<tr>
<th>Type of nozzle</th>
<th>Active ingredient</th>
<th>Air in the respiratory zone</th>
<th>Air in the treatment zone after 10 m from the edge of the field</th>
<th>Air in zone of possible wear * after treatment time</th>
<th>1 hour</th>
<th>3 days</th>
<th>7 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Super Poly 110-04 (slotted sprayer)</td>
<td>azoxystrobin</td>
<td>&lt;0.001**</td>
<td>0.0015</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.003</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>cyproconazole</td>
<td>&lt;0.05</td>
<td>0.085</td>
<td>&lt;0.008</td>
<td>&lt;0.008</td>
<td>0.11</td>
<td>&lt;0.008</td>
</tr>
<tr>
<td>Guardian Air GA110-04 (injector sprayer)</td>
<td>azoxystrobin</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>cyproconazole</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.008</td>
<td>&lt;0.008</td>
<td>&lt;0.008</td>
<td>&lt;0.008</td>
</tr>
</tbody>
</table>

Notes: 1. * - the study was conducted at a distance of 100 m from the edge of the site; 2. ** - below the limit of quantitative determination of the method in the air of the working zone and atmospheric air.

**Table III.** The magnitude of the potential risk of hazardous exposure to the drug Amistar Extra 280 SC, hp for refuelers and tractor drivers when using different sawing technologies

<table>
<thead>
<tr>
<th>Type of nozzle</th>
<th>Active ingredient</th>
<th>Risk values</th>
<th>Proportion of percutaneous risk, %</th>
<th>Proportion of inhalation risk, %</th>
<th>Combined risk</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>R</td>
<td>TD</td>
<td>R</td>
<td>TD</td>
</tr>
<tr>
<td>Super Poly 110-04 (slotted sprayer)</td>
<td>Azoxystrobin</td>
<td>0.01</td>
<td>0.12*</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>Cyproconazole</td>
<td>3.4</td>
<td>46.2*</td>
<td>0.53</td>
<td>0.48</td>
</tr>
<tr>
<td>Guardian Air GA110-04 (injector sprayer)</td>
<td>Azoxystrobin</td>
<td>0.01</td>
<td>0.04*</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>Cyproconazole</td>
<td>3.4</td>
<td>13.6*</td>
<td>0.53</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Notes: 1. R – refueler; 2. TD – tractor driver; 3. * – the values of the risk when using a slit sprayer are significantly higher according to the Student’s criterion at p <0.05.
When assessing the complex risk for tractor drivers, a statistically significant difference was found for azoxystrobin \((p = 0.002)\) and cyproconazole \((p = 0.001)\) when using a slotted sprayer Super Poly 110-04 and injector Guardian Air GA110-04. The proportion of percutaneous risk in variants №1 and №2 was lower for all active substances than the proportion of inhalation risk. The values of the combined risk when using a slotted sprayer \((0.46 \pm 0.04)\) significantly exceeded the data obtained when using an injector one \((0.02 \pm 0.006)\).

**DISCUSSION**

The results of the analysis of the working area air of persons involved in the preparation of the working solution, filling the sprayer tank and application of Amistar Extra 280, SC indicate compliance with the concentration of active substances. But it should be noted that the concentration of active substances in the working area of the tractor driver when slotted application is higher. In the air of the wear zone at a distance of 10 m from the edge of the field on the leeward side, the concentration of azoxystrobin and cyproconazole was also higher in variant №1. It should be noted that even such a minimal difference may be decisive in the implementation of the risk of negative impact not only for professional contingents, but, for example, for the ecosystem (honey insects in the neighboring field) or workers in the neighboring field (who doing non-pesticide field work, of course, without personal protection means).

The results of visual analysis of water-sensitive paper cards in the variant №1 of field studies confirmed the presence of wear of microdroplets, which can cause loss of effectiveness of the formulation, impact on non-target objects and create a burden on the environment as a whole. This problem becomes especially relevant when applying pesticides in private farms or in areas where compliance with the protection zone is difficult.

The obtained results correlate with the data given in 3, 8, 10, 11, i.e. we can say about the advantage of injector sprays not only as “anti-drift”, but also as means of providing lower concentrations of active substances under the same conditions of application of formulations based on them.

The values of occupational risks in the complex and combined effects of azoxystrobin and cyproconazole in the studied application technologies indicate a statistically significant difference for tractor drivers of slotted and injector application. According to 1, 5, 12 the proportion of inhalation risk is higher for tractor drivers due to work during the disintegration of pesticides working solutions; and for refuelers the proportion of percutaneous risk prevails, as components of professional activity are unpacking, dosing pesticide and filling the sprayer tank. The obtained results are comparable with the literature data, but it should be noted that in studies with slotted sprayers complex and combined risks for tractor drivers are significantly higher than for tractor drivers with injector spraying and this difference is due to the high inhalation risk. From the point of view of working conditions safety, the use of injectors is more justified, especially in private farms, where the use of personal protective equipment is not controlled by the employer and is often ignored by workers.

**CONCLUSIONS**

1. It is established that in real conditions of carrying out treatment of soy by the Amistar Extra 280, SC formulation with the use of Guardian Air GA110-04 injectors and slotted Super Poly 110-04 in compliance with the recommended agronomic and hygienic regulations for safe application, there is no excess of hygienic standards in the air of the working and wear zone and it is proved that occupational risk does not exceed acceptable \((< 1)\).

2. Statistical analysis of the obtained results showed that the values of inhalation risk are significantly higher for tractor drivers when using slotted sprayers than in tractor drivers involved in the application of pesticides by injector sprayers \((p < 0.05)\). Values of the combined complex risk of application of the Amistar Extra 280, SC formulation for tractor drivers of variant №2 application were significantly lower than those for tractor drivers of variant №1.

3. Absence of even insignificant wear of active substances of the investigated formulation outside of the processed field at use of injector sprayers is shown. This, on the one hand, will provide greater biological and economic efficiency of the formulation application by this method; on the other hand, it further reduces the risk of negative impact not only on the pesticide treatment workers, but also on other people and the ecosystem as a whole.

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The Authors declare no conflict of interest.

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