



## Research Article

# Damu-Safen pesticide exposure risk assessment, EC (fomesafen, 250 g/l)

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## Abstract

Annually the list of pesticides is replenished by new ones. One of the main criteria for their registration is toxicological and hygienic assessment and its impact on the environment.

In order to register the new soy herbicide Damu - Safen, EC (fomesafen, 250 g/l) it was necessary to assess its toxicological and hygienic impact on the environment and humans. Therefore, for the first time we conducted studies of the environmental objects under the influence of Damu-Safen, EC (fomesafen, 250 g/l) and the risk assessment of the active substance fomesafen and pesticide Damu - Safen, EC on the workers. According to the results of the assessment of working conditions for the workers of the tanker and the tractor operator, an acceptable risk was obtained that meets regulatory and hygienic requirements. Residual amounts of fomesafen not exceeding the normative levels were found during conducted studies on environmental objects.

Consequently, the results of the risk assessment in the application of pesticide Damu-Safen, EC (fomesafen, 250 g/l) and its impact on the working people and environmental objects indicate the possibility of its application in compliance with optimal environmental conditions and compliance with regulations for appliances and personal protective equipment.

## Introduction

Currently Kazakhstan is a country with a developed agricultural sector. Since Soviet times, cereals have prevailed among crops, in particular wheat and barley. Along with the development of new technologies in the agricultural sector, the cultivation of legumes such as soybeans, lentils, and peas has become actual. Kazakhstan today is a country with a developed agricultural sector. In this regard, there was the issue of the need to use safe pesticides for growing crops. Pesticides are anthropogenic pollutants of the environment and food in the world. There is a need to explore the dangers to public health and its environment in violation of the rules for the safe handling of pesticides. It is necessary to conduct a risk assessment for the safe use of the pesticide, working personnel and the public. Toxicological and hygienic assessment of pesticides is one of the main criteria for registration of pesticides in the territory of the States members of the Customs Union [1].

One of the main points of the criterion for toxicological and hygienic assessment of a pesticide is safe working conditions during its use, respectively - this is conducting a risk assessment for occupations whose work is associated with pesticides. Therefore, we assessed the impact of the pesticide Damu - Safen, EC (fomesafen, 250 g/l) for workers, and environmental objects (air of the working area, atmospheric air, soil layer of the earth and crop production), which is registered for the first time in the Republic of Kazakhstan.



Pesticide Damu - Safen, EC (fomesafen, 250 g/l) is a contact selective herbicide which is aimed to combat dicotyledonous weeds on crops of soybeans, beans in the post-emergence period.

The degradation of fomesafen in soils occurs mainly due to microbial activity. Although it is little known about the kinetic and metabolic behavior of this herbicide [2]. As well as fomesafen is a selective herbicide for ordinary leguminous plants.

Toxicological characteristics of the active ingredient fomesafen

Evaluation of acute oral toxicity.

(LD<sub>50</sub>) - Average lethal dose - the half lethal dose for rats was set at 1250 mg/kg

Evaluation of acute dermal toxicity

LD<sub>50</sub> acute dermal: for rats more than 1000 mg/kg

Inhalation toxicity

Acute inhalation: LC<sub>50</sub> (at 4 hours exposure) for rats 4.97 mg/m<sup>3</sup>

Irritation of the skin and mucous membranes:

Irritant effect of fomesafen 95% was studied on white rabbits the substance was applied to trimmed prepared skin on one side of the body, and covered with gauze bandages. The other side of the torso served as a control area on which distilled water was applied. The skin reaction was checked after 1 hour, 24 hours, 48 hours, up to 14 days after removing the dressing. According to the results of an average assessment of the degree of irritation, according to the intensity of erythema and edema, it was found that fomesafen irritates the skin of rabbits in the form of erythema for 1 hour, which then disappears for the next 24 hours; that indicates weak irritation of the skin of fomesafen.

The study of eye irritation off Fomesafen 95.0% was conducted on adults of the New Zealand White rabbits, which caused the appearance of 0.1 g of the test substances, which are released in the conjunctival sac of the right eye of each animal, the left eye served as a control in assessing eye irritation. Eye irritation was evaluated at approximately 1, 24, 48, 72 hours and 4, 7 days after application. Mortality, clinical signs and eye irritation were observed during the entire study period. The highest average value of eye irritation (the average score on the cornea, iris and conjunctival sac) was 12.5 after application. On the basis of this result and the criteria for the gradation of irritation, the test substance fomesafen under the experimental conditions of this study is moderately irritating to the eyes.

Sensitization: Sensitizer (guinea pigs) - poor sensitization has been noted.

According to toxicological and hygienic characteristics, fomesafen belongs to the 2nd hazard class according to WHO classification, the exposure is general toxic.

Hygienic standards of residual amounts of fomesafen in environmental objects and food.

ADD (Available daily dose) – 0,003 mg/kg

MAC water reservoirs – 0,0001mg/dm<sup>3</sup>

EAC (Estimated available concentration) soil -0,05 mg/kg

MAC air of the working area – 2,0 mg/m<sup>3</sup>

EAC (Estimated available concentration) in atmospheric air-0,003 mg/m<sup>3</sup>

MRL (mg/kg) – soybeans - 0.02; grapes, citrus fruits, pears, apples, fruits of corn, stone fruits - 0.01; nuts (almonds, cashews, chestnuts, coconuts, pistachios) -0.02

### The aim

- to assess environmental and handler safety as the pesticide Damu - Safen, EC (fomesafen, 250 g/l) is used as directed.

### Goals

- to assess the effect of the active ingredient fomesafen and the Damu-Safen pesticide EC (fomesafen, 250 g/l) in the air of the working area and its surroundings.
- to determine the effect of the active substance fomesafen in the water for household use (irrigation canal).
- to study residual amounts of fomesafen in the soil layer after its application.
- to conduct a study on the determination of pesticide residues in soybean leaves.

To conduct a study of the working conditions of working people and assess the risk of exposure of the pesticide fomesafen to working people and environmental objects, the subjects were instructed and agreed to the experiment.

The basis for the experiment were experimental fields located on the territory of LLP "Kazakh Research Institute of Agriculture and Plant Growing." In Almatybak Karasay district of Almaty region.

### Materials

- air samples of the working area, selected according to SS 12.1.005-88 "General sanitary and hygienic requirements for working area air" [3].
- washings from the skin surface of the open parts of the body and from the working clothes of the tanker and tractor operator working were carried out in accordance with Methodical recommendations No. 3056-84 "Development of methods for determining harmful substances on the skin" [4], Guidelines 1.2.3017-12 "Exposure risk assessment pesticides on workers" [5], Guidelines 4.1.3220-14 "Hygienic and analytical control over contamination of the skin of people working with pesticides".
- soil sampling was carried out in accordance with Sanitary Rules and Regulations 4.01.001-97 "Unified rules for sampling agricultural products, foodstuffs and the environment for the determination of trace quantities of pesticides", Almaty, 1997 [6].
- household water samples.

#### Calculations and formulas

$$D_f = D_{av} \times F \div F_1 \quad (1)$$

$D_f$  - actual skin exposure, mg/sm<sup>2</sup>

$D_{av}$  - the average content of the substance on the skin (dermal exposure) determined during a particular study, mg/sm<sup>2</sup>;

$F$  - the daily rate of the treatment area (ha) or the duration of the work shift (h).

$F_1$  - treatment area (ha) or the amount of seed treated (t), or work time (hours) during the study.

$$SC_{INH} = I_{mean} \div MAC / ISLE_{Iwa} \quad (2)$$

$SC_{INH}$  - safe coefficient of the substance inhalation exposure factor

$I_{mean}$  - fomesafen content of the substance in the working area air

MAC- maximum available concentration in the working area air

ASLE–approximately safe level of exposure in the workplace air

$$SC_{DER} = D_f \div MRL / EAL_{COS} \quad (3)$$

$SC_{DER}$  - safe dermal exposure coefficient

$D_f$  - dermal factor exposure, mg/cm<sup>2</sup>;

MRL – maximum permissible level of skin exposure

$EAL_{COS}$  - estimated acceptable level of contamination of the skin

$$Lim_{ch}^c \times M \times C_{RES} \times C_{REL}$$

$$EAL_{COS} = \frac{\quad}{S \times C_s} \quad (4)$$

$S \times C_s$

$EAL_{COS}$  - estimated acceptable level of contamination of the skin

$Lim_{ch}^c$  –threshold dose established experimentally in a chronic experiment or calculated on the basis of  $LD_{50}^K$  (mg/kg)

M – Human body weight on the average, taken as 70 kg.

$C_{RES}$  – the residual coefficient, which expresses the exposure ratio of the amount of a substance remaining on the skin after a certain time, and initially applied; on average 0.25.

$C_{REL}$  –The coefficient of relative permeability of the skin of a person and a rat or rabbit for a given substance (experimentally established) is approximately equal to 2.

S – Human skin area, on average = 16120 cm<sup>2</sup>

$C_s$ - the safety coefficient is determined by the hazard class for acute dermal exposure in accordance with the hygienic classification of pesticides.  $C_s$  for substances of 1-2 hazard classes for acute skin toxicity according to the hygienic classification of pesticides is from 20 to 10, for substances of 3-4 classes is from 10 to 3. For substances with pronounced distant or specific effects, including sensitization (1-2 hazard class),  $C_s$  can be taken at a level of 20 or more, for substances with carcinogenic properties (hazard class 2)  $C_s$  is equal to 50.

$$Lim_{ch}^c = K \cdot LD_{50}^K \quad (5)$$

$Lim_{ch}^c$  –threshold dose established experimentally in a chronic experiment or calculated on the basis of  $LD_{50}^K$  (mg/kg)

K – The coefficient for substances of hazard class 1-2 for acute dermal toxicity is 0.0002; for substances of hazard class 3-4 is 0.001

*The risk of complex effects of pesticides on the body of workers is determined by the value of the total safety coefficient ( $SC_{SUM}$ ) according to the formula for total toxicity:*

$$SC_{SUM} = SC_{INH} + SC_{DER} \quad (6)$$

$SC_{SUM}$  - safety coefficient sum

$SC_{INH}$  - safe coefficient of the substance inhalation exposure factor

$SC_{DER}$  - safe dermal exposure coefficient

$$SC_{SUM} \leq 1 \quad (7)$$



### Instruments and equipment

- Air sampler automatic - Model OP -442 TC, Russia, primary calibration, May 18, 2017.
- Liquid chromatograph WatersBreeze 2, serial number K1687E232A, manufactured in the USA, 2016, calibration certificate No. VA 09-19-4974 of 05.12.2017.
- Analytical Scales AX 120, NPV 120g, "Shimadzu", Japan, calibration certificate №VA-02-02-29825 of 19.04. 2017.
- Scales "MWP-150N" "CASCORPORATION", NPV 150g, South Korea, calibration certificate №VA-02-02-29824 of 19.04.
- Tractor "Belarus MTZ -82" with a pole sprayer, made in China, exciting length of treatment 16 m.
- Personal protective equipment.

### Methods for determining residual amounts of fomesafen

Determination of residual amounts of fomesafen in environmental objects was carried out by high performance liquid chromatography using a Waters Breeze 2 chromatograph as described in the HPLC method in the proposed article using SLE/LTP and HPLC / AD [7].

- Determination of residual amounts of fomesafen in the air of the working area was carried out according to Guidelines No. 6218-91 "Methodological guidelines for the measurement of chlorofluazuron concentrations in the air of the working area" [8], thus this pesticide is close by empirical and molecular formula to fomesafen.
- Determination of fomesafen in water was carried out in accordance with Guidelines No. 2365-81 "Methodological guidelines for the determination of phenylurea herbicides (phenuron, koran, thomilon, monuron, diuron, dicouran, doxex, tenor n, faloran, and rubbers, li nori, patoran, lowran) in water, soil, plant material, vegetables, and, by definition, herbicides (arezin, linuron, patoran, maloran) and their metabolites — aromatic amines — in water when combined by gas-liquid chromatography" [9].
- In the soil, the determination of fomesafen was carried out according to the developed method "Methodological guidelines for the determination of residual amounts of fomesafen in soybean, soybean oil and soil by high performance liquid chromatography", developed by specialists of SPC (scientific practical center) TAU.

### Results

For full assessment of the risk Damu - Safen, EC (fomesafen, 250 g/l) we selected 72 air samples from the working area, 16 samples from the atmospheric air, 10 samples water, 16 samples soils also we selected 38 swabs from the tanker and operator (Table 1).

#### Determination of fomesafen in the air of the working area

The sampling of air in the working area was carried out directly during the treatment of the field with the preparation "Damu-Safen, EC (fomesafen, 250 g/l)" according to Guidelines No. 6218-91" Guidelines for the measurement of chlorofluazuron concentrations in the air of the working zone" [8].

Samples were taken in the breathing zone of a tanker and a tractor driver –



**Table 1:** The number of samples taken during Damu - Safen, EC (fomesafen, 250 g/l)

Number of sampling points	The number of samples of environmental samples	Number of sampling points	The number of samples of environmental samples	The number of points of the washings from the tanker	The total number of swabs from the tanker	The number of points of the swabs from the tractor operator	The total number of swabs at the operator
1	2	3	4	5	6	7	8
Water from the aryk		working area air for the tanker		5	16	7	22
3	10	7	36				
soil		working area air for the operator					
5	16	7	36				
		Atmospheric air					
		3	16				
Total number							
8	26	25	114	5	16	7	22

operator of production conditions. During the shift at individual stages of the process at one point, five air samples were taken from the working area. It was taken the average values in each stage.

The results of the determination of the content of pesticide in the air of the working area are presented as an arithmetic average exposure (Figures 1,2).

I<sub>mean</sub> –the average content of substances in the air of the working area among the samples taken during a single operation.

### Determination of fomesafen in the atmospheric air

The atmospheric air samples were taken in five replications from 3 points. The average is taken from each sampling point (Table 2).

The concentration of fomesafen in atmospheric air was 0.00135 mg/m<sup>3</sup>. PELs in the atmosphere air -0.003 mg /m<sup>3</sup>

### Determination of residual amounts of fomesafen on the skin of working people

The swabs were carried out at the end of work with open and closed overalls and other means of individual protection of the skin. Washout was performed by washing the fixed area of the skin with a washing liquid (80% ethyl alcohol) using a standard-sized tissue cloth (specially prepared earlier) and tweezers (2-fold washing from top to bottom), then the washout was placed in a glass container with a lid.

Based on the value of D<sub>a</sub>, the actual skin exposure of D<sub>p</sub> mg/cm<sup>2</sup> is calculated, taking into account the work during the work shift according to the formula:

$$D_f = D_a \times F \div F_1 \quad (1)$$

$$D_f = 0,000020484 \times 1 \div 2 = 0,00001024$$

The actual skin exposure of D<sub>p</sub> mg/cm<sup>2</sup> was determined taking into account the ratio of the work time during the study within an hour and the duration of the work shift with pesticides in the field was 2 hours for the tanker (Figure 3).

D<sub>a</sub> – the average content of the substance on the skin (dermal exposure) determined during a particular study, mg/sm<sup>2</sup>;

F –the daily rate of the treatment area (ha) or the duration of the work shift (h), for the tanker, the duration of the work shift, taking into account the number of gas stations per shift (if necessary, the duration of each of them).

F<sub>1</sub> – treatment area (ha) or the amount of seed treated (t), or work time (hours) during the study.

Based on the  $D_a$  value, according to formula and taking into account the work during the work shift the actual skin exposure  $D_p$  mg/cm<sup>2</sup> is calculated

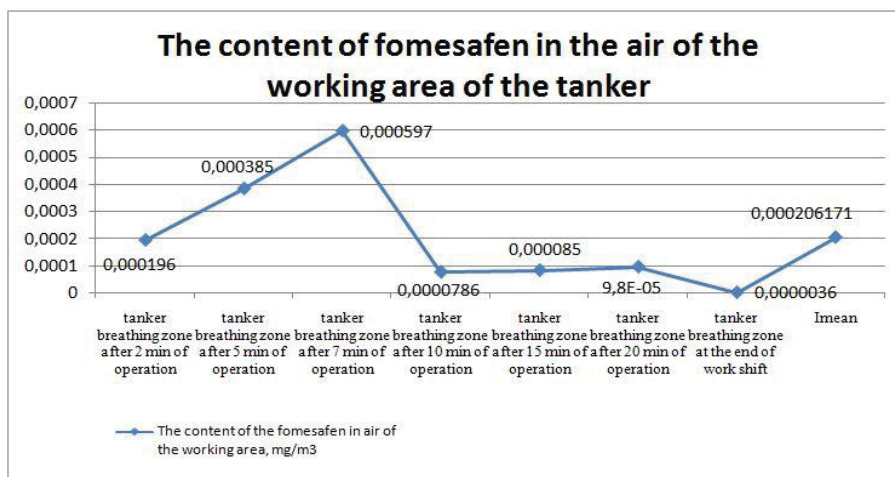
$$D_f = D_a \times F \div F1 \quad (1)$$

$$D_f = 0,000001936 \times 6 \div 2 = 0,000005808$$

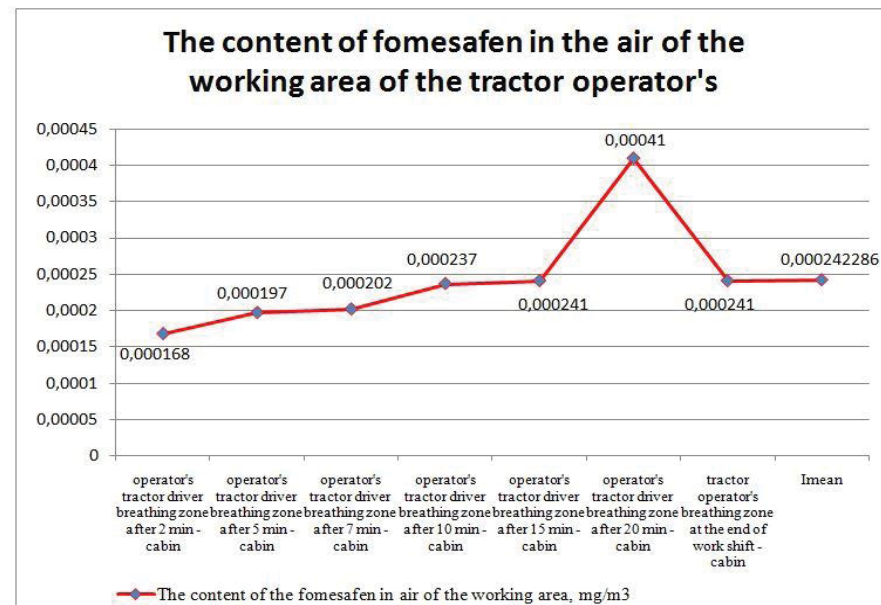
The actual skin exposure of  $D_p$  mg/cm<sup>2</sup> was determined taking into account the ratio of work time during the study within 2 hours and the duration of the work shift with pesticides in the field was 6 hours for the operator (Figure 4).

**Table 2:** The level of fomesafen in atmospheric air after spraying.

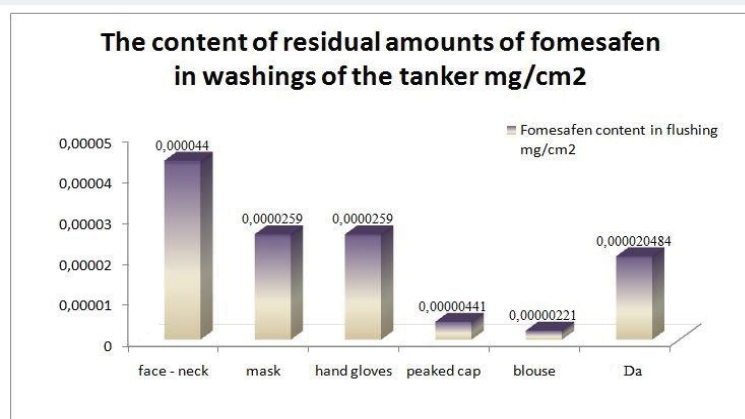
The sampling place	Spray radius	Mg/m <sup>3</sup> value
The first point	100 M	0,00366
The second point	200 M	0,000289
The third point	300 M	0,000112
The average		0,00135



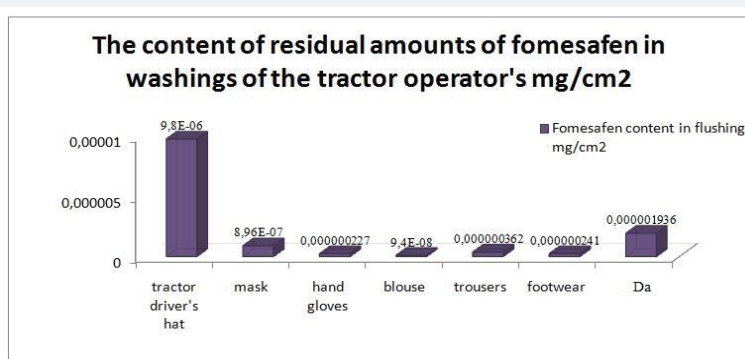
**Figure 1:** The content of fomesafen in the air of the working area of the tanker.



**Figure 2:** The content of fomesafen in the air of the working area of the tractor operator's.



**Figure 3:** The content of residual amounts of fomesafen in washing of the tanker.



**Figure 4:** The content of residual amounts of fomesafen in washing of the operator's tractor.

To assess the risk, we determine the ratio of the actual inhalation and dermal exposure and hygienic standards used as an acceptable level of inhalation and dermal exposure;

a) *The risk of inhalation exposure* is determined by the value of the safety factor for inhalation intake of pesticides.

$$SC_{INH} = I_{mean} \div \frac{MAC}{ISLE_{iwa}} \quad (2)$$

$$SC_{INH} = 0,000206171 \div 2 = 0,00010 - \text{tanker}$$

$$SC_{INH} = 0,000242286 \div 2 = 0,00012 - \text{operator - tractor driver}$$

MAC of fomesafen in the air of the working area – 2,0 mg/m<sup>3</sup>

ISLE<sub>iwa</sub> - indicative safe levels of exposure to pollutant substances in working areas

b) *The risk of dermal exposure* is determined by the value of the safety factor for skin entrance of pesticide SC<sub>DER</sub>, mg/cm<sup>2</sup>, determined by the ratio of the actual skin exposure of the substance D<sub>f</sub> (mg/cm<sup>2</sup>) to MRL (mg/cm<sup>2</sup>) or EAL<sub>cos</sub> mg/cm<sup>2</sup> by the formula:

$$SC_{DER} = D_f \div MRL / EAL_{cos} \quad (3)$$

$$SC_{DER} = 0,00001024 \div 0,00434 = 0,00235 \text{ (tanker)}$$

$$SC_{DER} = 0,000005808 \div 0,00434 = 0,00133 \text{ (operator - tractor driver)}$$



Approved  $MRL_{COS}$  values are used as permissible levels of pesticide content on the skin. For pesticides that do not have  $MRL_{COS}$  on the skin, the calculated value of EAL of skin contamination ( $EAL_{COS}$ ). Is used as a hygienic standard.

c) *The calculation of the estimated acceptable level of contamination of the skin  $EAL_{COS}$*

The  $EAL_{COS}$  ( $mg/cm^2$ ) calculation ( $mg/cm^2$ ) is carried out using the  $Lim^c_{ch}$  value ( $mg/kg$ ), experimental or calculated on the basis of the acute dermal toxicity index  $LD_{50}$  ( $mg/kg$ ).  $EAL_{COS}$  is calculated by the formula:

$$EAL_{COS} = \frac{Lim^c_{ch} \times M \times C_{RES} \times C_{REL}}{S \times C_S} \quad (4)$$

$$Lim^c_{ch} = K \cdot LD_{50}^K \quad (5)$$

$$Lim^c_{ch} = 0,0002 \cdot 1000 = 0,2$$

Fomesafen is classified as hazard class 2,  $LD_{50}$  skin - 1000 mg/kg

$$EAL_{COS} = 0,2 \times 70 \times 0,25 \times 2 \div 16120 \times 10 = 0,00434$$

d) *The risk of complex effects of pesticides on the body of workers is determined by the value of the total safety coefficient ( $SC_{SUM}$ ) according to the formula for total toxicity:*

$$SC_{SUB} = SC_{INH} + SC_{DER} \quad (6)$$

$$SC_{SUM} = 0,00010 + 0,00235 = 0,00245 \text{ (tanker)}$$

$$SC_{SUM} = 0,00012 + 0,00133 = 0,00145 \text{ (operator – tractor driver)}$$

### The content of residual amounts of fomesafen in water for domestic use

Next to the test field at a distance of 150 meters there is an irrigation canal for household use. Sampling was done by samplers. The concentration of fomesafen was 0.000032 mg/dm<sup>3</sup>. MAC of fomesafen in the water of reservoirs was 0.0001 mg/dm<sup>3</sup>.

### The residual content of fomesafen in the soil

A sampler was used to determine the residual amounts of fomesafen in the soil. The content of fomesafen in the soil after spraying was completed 30 minutes after treatment was 0.018 mg/kg with MAC of fomesafen in the soil - 0.05 mg/kg.

## Discussion

The risk of integrated receipt of pesticides is considered acceptable if

$$SC_{SUM} \leq 1 \quad (7)$$

$$SC_{SUM} \leq 0,00245 \text{ (tanker)}$$

$$SC_{SUM} \leq 1$$

$$SC_{SUM} \leq 0,00145 \text{ (operator – tractor driver)}$$

In the case of elevated concentrations of substances in the air of the working area ( $SC_{INH} \geq 1$ ) when calculating the risk, it is necessary to consider the degree of respiratory protection according to the technical characteristics of the type of respirator used or established experimentally.



$SC_{SUM}$  (the value of the total safety factor) for the tanker when using fomesafen as part of the pesticide "Damu – Safen, EC (fomesafen, 250 g/l) "amounted to  $0.00245 \leq 1$  - risk acceptable.

The content of fomesafen in the soil after spraying in 30 minutes and after treatment was 0.018 mg/kg with MRL of fomesafen in the soil -0.05 mg/kg.

During the study of atmospheric air, next to the site of spraying, the concentration of fomesafen was 0.00135 mg/m<sup>3</sup> with a PELs in the air of the atmosphere amounted to 0.003 mg/m<sup>3</sup>. The content of fomesafen in the water for household purposes (irrigation canal) was 0.000032 mg/dm<sup>3</sup>; when MRL, the water of reservoirs was 0.0001 mg/ m<sup>3</sup>.

Thus, it was concluded that the danger of the complex (inhalation and dermal) effects of the pesticide Damu-Safen, EC (fomesafen, 250 g/l) when applied comply with hygienic standards.

## Conclusion

According to the results of the assessment of working conditions for workers of the tanker and the tractor-machine operator, an acceptable risk equal to 0.00245 for the tanker and 0.00145 for the tractor operator-0.00145 in pesticide Damu-Safen was received, (Fomesafen, 250 g/l), that is evidence of the possibility of registering a pesticide for further use in the territory of the Republic of Kazakhstan.

The results of the risk assessment for the use of pesticide Damu-Safen, EC (fomesafen, 250 g/l) and its impact on workers and environmental objects (air of the working area) indicate the compliance of the results with the hygienic requirements of the Customs Union.

Based on the results of the risk assessment of exposure to the active ingredient fomesafen in Damu-Safen, EC (fomesafen, 250 g/l) prove the possibility of use in compliance with optimal environmental conditions and compliance with the rules of application and personal protective equipment for the observer.

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