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ORIGINAL ARTICLES

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SUBSTANTION OF THE NEED FOR MONITORING IN ENVIRONMENTAL OBJECTS OF INSECTICIDES FROM THE CLASS OF TETRAMIC AND TETRONIC ACID DERIVATIVES TAKING INTO ACCOUNT THEIR SPECIFIC INFLUENCE ON THE HUMAN ORGANISM

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ABSTRACT

The aim: Substantiation of the need for monitoring in environmental objects of spiromesifen, spirodiclofen and spirotetramat, taking into account their specific impact on the human organism to reduce the risk of their negative influence on public health and the environment.

Materials and methods: The subject was insecticides, the class of tetramic and tetronic acids derivatives, spiromesifen, spirodiclofen and spirotetramate. Physico-chemical, toxicological and hygienic evaluation of the results was performed according to the literature data. Selection criteria were used to substantiate the needs in monitoring of these insecticides.

Results: Spiromesifen, spirodiclofen and spirotetramate according to the Hygienic classification of pesticides by the limiting criterion of hazard belong to 1 class (strong allergen), 2 (carcinogen) and 3 classes (inhalation toxicity), respectively. The value of ADD (allowable daily dose) for human of spiromesifen, approved in Europe is 0.03 mg•kg-1. According to the assessment of hazards for professional contingents and the coefficient of possible inhalation poisoning (CPIP) and the coefficient of selective action (CSA), spiromesifen may pose a risk. We can conclude about the safety of the compound according to GUS, SCI-GROW, LEACH indices, and hence the absence of risk of potential entry of the substance into the human body with contaminated water or food. According to persistence in the environment, these insecticides are law and moderately persistent. Direct effect on the thyroid gland is absent.

Conclusions: Monitoring of spiromesifen and spirotetramate in water, soil and agricultural raw materials is not obligatory, and for spirodiclofen is desirable.

KEY WORDS: Insecticides, Toxicology, Monitoring, Risk

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INTRODUCTION

The application of pesticides in agriculture in all countries of the world is now a necessary part of successful crop production and profits with minimal losses [1]. However, the question of uncontrolled and mass chemical plant protection products usage is very acute, given their accumulation and the studied toxic effects on the environment and the human organism [2, 3].

Every year, new modern, more effective formulations appear on the chemical market [4]. Insecticides derived from tetramic and tetronic acids – spiromesifen, spirotetramat and spirodiclofen are among those that have proven themselves in the effective control of pests and are widely used in Ukraine and Europe [5]. This new chemical class combines two mechanisms of action on the warm-blooded animals and humans: induction of liver microsomal enzymes and inhibition of 4-hydroxyphenylpyruvate dioxygenase [5].

Monitoring and risk assessment for the population and professional contingents when consuming and working directly with pesticides is used by all European countries and the United States [6, 7]. However, the vast majority of monitoring models do not take into account specific indices for pesticides that can affect the thyroid gland, cause endocrine disorders and increase the already high level of endocrine pathology, including the thyroid gland, in the world [8].

Therefore, the introduction of monitoring methods is quite relevant, necessary and timely to reduce the risk of adverse effects of the above insecticides on the environment and the human organism.

THE AIM

The aim – substantiation of the need for monitoring in environmental objects of spiromesifen, spirodiclofen and spirotetramat, taking into account their specific impact on the human organism to reduce the risk of their negative influence on public health and the environment.

MATERIALS AND METHODS

Representatives of insecticides of tetramic and tetronic acids derivates class were selected for the study: spiromesifen, spirodiclofen and spirotetramate.

Table I. Physico-chemical properties of spiromesifen, spirodiclofen and spirotetramate [9, 14, 15]

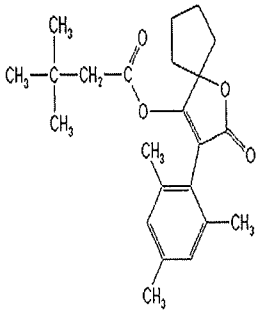
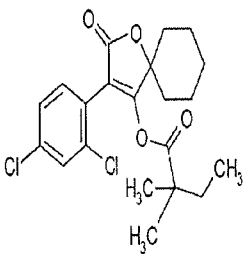
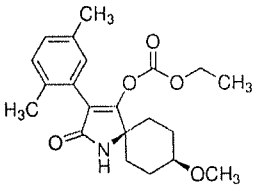
Index	Spiromesifen	Spirodiclofen	Spirotetramate
Empirical formula	C23H30O4	C21H24Cl2O4	C21H27NO5
Relative molecular weight	370.48	411.32	373.48
Vapor pressure (at 20 ° C), mPa	7×10-3	3×10-4	5,6×10-6
Melting point, °C	98.0	94.8	142.0
Solubility in water (at 20 °C), mg·l-1	0.13	0.05	30.0
Partition coefficient n-octanol / water (logKo/w)	4.55	5.83	2.51
Chemical formula			
Solubility in organic solvents, g·l-1	heptane - 23, acetone, xylene, ethyl acetate - 250	heptane - 20, acetone, xylene, ethyl acetate -> 250	ethanol - 44, toluene - 60, acetone -, 100-120, ethyl acetate - 67

Table II. Selection criteria for monitoring of insecticides

Index of hazard	Selection criteria	Object for controle			
		air	water	soil	food products
Physico-chemical properties					
Vapor pressure, mPa	>1×10-4	+	-	-	-
Solubility in water, mg·l-1	>100	-	+	-	-
Soil sorption coefficient (Koc)	<75/>500	-	+	+	-
Toxicological danger					
Class of hazard	I-II клас	+	+	+	+
Allowable daily dose (ADD), mg·kg-1	<0,01	+	+	+	+
Coefficient of possibility of inhalation poisoning (CPIP)	>2,0	+	-	-	-
Selective action coefficient (SAC)	<99	+	-	-	-
Occupational risk (complex, combined)	>1	+	-	-	-
Persistence in the environment and ecotoxicological hazard					
Half-life period (DT50) in soil, day	>30	-	-	+	-
Ecotoxicological hazard (Ecotox)	>0,4	-	-	+	-
DT95 in water, day	>10	-	+	-	-
Ground ubiquity score (GUS)	>1,8	-	+	-	-
Risk of pesticides intake with water in case of their leaching from soil to groundwater	>1	-	+	-	-
DT50 in agricultural raw materials, day	>14	-	-	-	+

The main physical and chemical properties are given in the Table I [9].

The criteria proposed in [10, 11, 12] for fungicides and adapted for insecticidal compounds were used to preliminarily assess the need to monitor the proposed substances in the environment.

The selection criteria for monitoring insecticides (on example of spiromesifen) include the physicochemical properties of the compound, toxicological and ecotoxicological hazards, and, of course, stability in the environment (Table II).

The coefficient of sorption (Koc) of spiromesifen in the soil is 30,900, the allowable daily dose (ADI) is 0.03 $mg \cdot kg^{-1}$ [9].

According to the literature [9], the half-life period (DT_{50}) in the soil of spiromesifen is 4.1 days, DT_{50} in water – 0.3,

Table III. Selection of investigated insecticides for hygienic monitoring [5, 9, 14, 15, 18]

Compound	Index name and value (score in points)											
	Allowable daily dose (ADD), mg/kg	Class of hazard according to State Standards 8.8.1.002-98	Impact on the thyroid gland as a target organ	The severity of pesticide-induced tyrosinemia (plasma tyrosine levels, nmol/ml)	Half-life period (DT50) in soil, day	Half-life period (DT50) in water, day	Half-life period (DT50) in plants, day	the Groundwater and Surface Water Pollution Index (LEACH), units	Screening of maximum pesticide concentration in groundwater (SCI-GROW), µg·l-1	Integrated index of pesticides contaminated water consumption (IIPCWC)	Integrated index of pesticides contaminated food consumption (IIPCFC)	Total score
Spiromesifen	0,03 (1)	1 (4)	Weak effect in animal experiments (2)	<300 (1)	4,1 (1)	0,15 (1)	2,0 (1)	0,00002 (1)	5,35×10-3 (2)	3 (1)	4 (1)	16
Spirodiclofen	0,001 (4)	2 (3)	Weak effect in animal experiments (2)	<300 (1)	7,0 (1)	0,7 (1)	10,1 (2)	0,00001 (1)	5,35×10-3 (2)	6 (2)	8 (3)	20
Spirotetramate	0,05 (1)	3 (2)	Weak effect in animal experiments (2)	<300 (1)	0,19 (1)	0,78 (1)	3,0 (1)	0,01972 (2)	2,05×10-4 (2)	4 (1)	4 (1)	15

DT_{50} in agricultural raw materials is 2.0 days. The value of GUS (ground ubiquity score) is equal to 0.06.

Given that compounds of this class can affect the functioning of the thyroid gland [5], an assessment of the need for their monitoring was carried out taking into account this feature according to the criteria given in [13].

RESULTS

According to the generalized data of the literature [5, 14, 15] new chemical compounds – insecticides of the tetramic and tetronic acids derivates class – spiromesifen, spirotetramat and spirodiclofen have two types of effects on warm-blooded animals and humans: induction of microsomal liver enzymes and inhibition of 4-hydroxypyruvate dioxygenase.

All three active substances, according to the Hygienic classification of pesticides according to the degree of hazard (StateStandard 8.8.1.002-98) [16], by the acute oral and dermal toxicity belong to the 4th class of hazard, and inhalation toxicity – to the 3rd class of hazard [5, 14, 15]. Spiromesifen, same as spirodiclofen, is not an irritant to the skin and mucous membranes of the eyes – hazard class 4. Spirotetramate [5, 14, 15] by irritating effect on the skin also belongs to the 4th class of hazard, but by irritating effect on mucous membranes belongs to the 3rd class (slightly irritating). Spiromesifen, in contrast to spirodiclofen (hazard class 2) and spirotetramate (hazard class 3), is a strong allergen – hazard class 1. According to mutagenic activity, all substances belong to the 4th hazard class. Spirotetramate [5, 14, 15]is not a carcinogen – hazard class 4, in contrast to spiromesifen – hazard class 3 and spirodiclofen – hazard class 2. According to embryo- and reproductive toxicity, spiromesifen, spirodiclofen and spirotetramate belong to the 3rd class of hazard [5, 14, 15].

According to the limiting criteria of toxicity, spiromesifen is the most toxic and belongs to the 1st class of hazard – a strong allergen, spirodiclofen [5, 14, 15] belongs to the 2nd class by carcinogenic effect, and spirotetramate – to the 3rd class of hazard (acute inhalation toxicity).

According to the physicochemical properties, spiromesifen has a low sorption capacity (Koc), is not mobile and is moderately soluble in water (Table I). The value of the allowable daily dose (ADI) characterizes it as a low-risk compound for the human body [5].

The test compounds does not have high possibility of inhalation poisoning (according to CPIP) and the coefficient of selective action (CSA), and have allowable occupational risk level (complex and combined). So, according to Table II there is no need for their obligatory monitoring in air.

Spiromesifen is not stable in environmental conditions and is characterized by an extremely low possibility of leaching into groundwater by the value of GUS [5], so it does not pose a potential risk when using contaminated food and water. However, according to Table II its ecotoxicological hazard, and the existing risk of the pesticide entering the water, which washes the chemical from the soil into the groundwater, should be taken into account.

Monitoring of pesticides in Ukraine and Europe with an increased risk of thyroid disease is necessary and relevant [6, 11]. For example, the incidence of thyroid pathology among the population of Ukraine is the highest in Kyiv region [17], but regions that are intensively engaged in agriculture, and therefore actively use chemical plant protection products, also need such control and scientific substantiation of norms and regulations for pesticides application and their further monitoring.

According to the scale proposed [18], each criterion was evaluated in points and their total amount was calculated for each studied insecticide and analyzed by us (Table III).

Assessing the toxicological effects of tetramic and tetronic acids derivatives, namely spiromesifen, spirodiclofen, and spirotetramate on the thyroid gland, it can be concluded that the effect in animal experiments is weak; tyrosinemia induced by these pesticides is absent.

When studying the stability of spiromesifen in various environmental objects, it, like spirodiclofen and spirotetramate, is unstable in soil and water (class 4). According to stability in plants, spiromesifen is an unstable compound, same as spirotetramate (class 4), spirodiclofen is moderately stable (class 3).

According to the integrated index of pesticides contaminated water consumption (IIPCWC) and integrated index of pesticides contaminated food consumption (IIPCFC), spiromesifen and spirotetramate have as low-risk for humans (class 4), and spirodiclofen is moderately dangerous (class 3).

Analyzing the screening of the maximum concentration of pesticides in groundwater (SCI-GROW) of spiromesifen, spirodiclofen and spirotetramate, we can talk about insignificant and much lower than the permissible concentrations of pollution. The index of potential contamination of groundwater and surface water (LEACH) for all investigated insecticides (spiromesifen, spirodiclofen, spirotetramat) in different soil and climatic conditions is low.

From obtained results we can assess the need to monitor these pesticides of tetramic and tetronic acids derivatives class for the total score: spiromesifen and spirotetramate are insecticides for which monitoring in environmental objects is not obligatory (16 and 15 points, respectively), and spirodiclofen is subject to the desired monitoring (20 points) in water, soil and agricultural raw materials.

DISCUSSION

Among other classes of pesticides, insecticides have proven to be safer chemical plant protection products according to above assessed indices [19].

Comparing with literature data [20] insecticides of the tetramic and tetronic acids derivatives class, spiromesifen, spirotetramat and spirodiclofen, are safer in assessing groundwater pollution than previously studied herbicides dicamba, sulfoniculfonyl sequinilicin, pyraclostrobin, which are characterized by a high risk of contamination and may pose a risk to humans if they potentially enter the water through agricultural raw materials that have been treated with formulations with these active ingredients.

The fact that their monitoring in the air is not required and in water, soil and food is optional also testifies to the lesser danger of the studied compounds. In contrast, for most fungicides, monitoring in soil and food is mandatory; in water – also desirable [11-13].

Also, studied insecticides are lower or on the same level with a very widespread today SDHI fungicides in term of needs in monitoring, taking into account their possible effect on thyroid gland. For example, SDHI fungicides from the chemical class of pyrazolecarboxamides (isopyrazam, pentiopyrad, sedaxan, fluxapyroxad) are assigned to the second pesticide group, hygienic monitoring of which is desirable but not required [18]. This is due, to low environmental sustainability (same as for spiromesifen, spirodiclofen, spirotetramat) and to their low toxicity (despite of spiromesifen, spirodiclofen).

CONCLUSIONS

Based on the results obtained, spiromesifen and spirotetramate, can be classified as the first group of pesticides, hygienic monitoring of which in environmental objects is not obligatory, spirodiclofen – to the second group of pesticides, hygienic monitoring of which in water, soil and agricultural raw materials is desirable, in air is not required.

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The Authors declare no conflict of interest.

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