

Assessment of spiromesifen peculiarities of migration into groundwater and surface water and prediction of risks to human health when using such water for drinking purposes

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Objective: To study the peculiarities of the migration of spiromesifen into groundwater and surface water and to predict the risks to human health when using such water for drinking purposes.

Methodology: Field experiments to study the dynamics of residual amounts of spiromesifen, its stability and behavior in the soil after fan spraying of apple orchard and vineyard were conducted in different soil and climatic conditions: Steppe, Forest-Steppe, Polissya. K_{oc} , GUS and $LEACH_{mod}$ were used to assess the migration capacity of the insecticide. To predict the risk, we used the integrated hazard vector of groundwater pollution (R) and an integral index of hazard of pesticide contaminated water consumption (IIHPCWC).

Results: The calculated value of GUS (-0.92) and

leaching index (3.3×10^{-5}) allow to pertain spiromesifen to a low level of risk of leaching into groundwater – hazard class 3. It was established that spiromesifen by persistency in soil in soil and climatic conditions of Steppe, Forest-Steppe, Polissya belongs to low-stability pesticides, and characterized by low mobility in soil.

Conclusion: It was shown that spiromesifen is a moderately hazardous substance for humans due to groundwater contamination (class 3) and low-risk (class 4) due to surface water contamination by the integral index of hazard of pesticide contaminated water consumption.

Keywords: Migration, groundwater, surface water, risks.

INTRODUCTION

The basis of the principles of any country state policy in the field of pesticides and agrochemicals is the priority of preserving human health and environmental protection in relation to the economic effect of chemical plant protection active ingredients (a.i.) and formulations.¹ According to WHO estimates, unintentional pesticide poisoning kills approximately 355,000 people worldwide each year.¹ Among the main routes of pesticides entering the human body are ingestion or intake of food and water, and the main source of pesticide formulations is agroecosystems.^{1,2}

Chemical Plant Protection Products (ChPPs) are characterized by low pedochemical activity – they practically do not enter into chemical reactions with the soil and do not affect its properties.^{2,3} Pesticides that get into the soil are absorbed by the root systems of plants, transported with soil moisture, absorbed by organic and mineral colloids, subjected to microbiological and photochemical decomposition.^{2,3} The migration of pesticides through the soil profile is due to the capillary-

gravitational movement of water. The speed and depth of their penetration depend on many factors related to soil and climatic features (particle size distribution, colloidal content and sorption capacity of soils, precipitation), and the properties and doses of the formulations themselves.¹⁻³

For the population that consumes water from wells, i.e., groundwater, as it lives in a decentralized water supply, this water, in contrast to the interstratal (middle) water is more likely to be potentially contaminated with pesticides.⁴ Therefore, the registration and implementation to agriculture of new ChPPs is preceded by a number of studies, experiments, interpretations and analysis of the results of researches on hygienic assessment of the potential risk of soil contamination and migration in the system “soil-groundwater and surface water sources” of a new compounds. The aim of our study was to study the peculiarities of the migration of spiromesifen into groundwater and surface water and to predict the risks to human health when using such water for drinking purposes.

METHODOLOGY

Field experiments were conducted during 2016 – 2021 in accordance with⁵ in different soil and climatic conditions: Steppe, Forest-Steppe, Polissya. The application of the insecticide Oberon Rapid 240 SC was carried out in: vineyards – in Odesa region, Ovidiopol district; apple trees – Kyiv region, Skvyr district, Pustovarivka village; corn – Poltava region, Poltava district, village Takhtaulove; sunflower – Mykolaiv region, Voznesenskyi district, Yastrubinovo. Method of treatment – fan spraying, crops – apple orchard and vineyard, consumption rate – 0.8 l/ha, twice.

Soil samples were taken by the “envelope” method at a depth of 10 – 15 cm in three repetitions for each sampling point (about 1 kg), packed in hermetically sealed containers and transported to the laboratory in a refrigerator, where they were stored in a freezer. The selection of samples was carried out by a group of certified specialists who were trained in “Requirements of the new edition of the ISO 17025: 2017 standard. Sampling uncertainty calculation – Theory and Practice”.

The stability of spiromesifen in soil was assessed according to State Standard 8.8.1.002-98 and the IUPAC International Classification.^{6,7} Following indices were used to assess the migration capacity of the insecticide: K_{oc} (organic carbon sorption constant), GUS (Groundwater Ubiquity Score) – potential leaching index, which shows the probability of migration from soil into ground water⁸ and $LEACH_{mod}$ (Leaching Estimation and Chemistry) – leaching index to assess potential contamination of ground water and river water.⁹ The migration ability of spiromesifen according to the K_{oc} constant was assessed using the SSLRS International Classification.¹⁰

However, all of the above indices allow the assessment of potential pesticide contamination of water only and do not take into account the risk that substances may pose to human health due to the consumption or commercial use of such contaminated water. Therefore, to predict the risk, we used the integral hazard vector of groundwater pollution (R) according to the method of Sergeyev et al¹¹ and an integral index of hazard of pesticide contaminated water consumption (IIHPCWC).¹²

Statistical Analysis: Processing of results was performed using the licensed software package IBM SPSS Statistics Base v.22.

RESULTS

The half-life of spiromesifen varies from a maximum of 21 days to a minimum of 1.9 days (Table 1), depending

on the above conditions. In all cases, according to the stability in the soil in accordance with and the test compound belongs to 3-4 hazard classes – moderately and low persistent. In the studied soil and climatic conditions τ_{50} of the test compound was 7.8 days, which allows to classify it according to the degree of persistence in the soil to low-persistent pesticides – hazard classes 4 and 3. Spiromesifen in terms of the sorption constant K_{oc} (Table 2) belongs to non-mobile substances (class 5) according to the International Classification of SSLRS.¹⁰

The value of GUS¹³ is -0.16, which indicates a very low⁸ or extremely low⁷ risk of potential leaching of spiromesifen in groundwater (Table 3). According to our research, the index of potential leaching of the substance in studied soil and climatic conditions is -0.92. The obtained result (Table 3) indicates a very low or extremely low risk of the study insecticide leaching to groundwater when using pesticide formulations based on it. Both GUS values allow the compound to be classified as hazard class 6 and with a score of 30 – to a low level of risk of pesticides leaching into groundwater (Table 3).

The leaching index ($LEACH_{mod}$) was calculated taking into account spiromesifen half-life in soil calculated based on own studies – 3.3×10^{-5} (Table 2). The risk of potential contamination is assessed as low (hazard class 3). The next step in our study was to calculate a possible risk of hazard spiromesifen effect after consumption of contaminated water. To do this, we used index of toxicity and cumulative properties of the substance – the zone of biological effect ($Z_{biol.ef}$):¹¹ $Z_{biol.ef} = 2000/14.2 = 140$ (according to¹³); $Z_{biol.ef} = 2000/6.5 = 307$ (own research, males); $Z_{biol.ef} = 2000/19.3 = 104$ (own research, females).

Chronic effect on oral administration was calculated for both males and females, the assessment was performed on a scale.¹¹ According to the hazard scale, and the zone of biological effect of spiromesifen for male rats and females was 50 points (Table 4). According to the defined zone of biological effect (Table 4) spiromesifen pertain to medium-hazardous pesticides.

The integral vector of hazard of groundwater and surface water contamination (R) was calculated according to the S.G. Sergeyev et al. method:¹¹

$$R = \sqrt{30^2 + 50^2 + 50^2} = 76.8 \text{ (groundwater);}$$

$$R = \sqrt{30^2 + 30^2 + 50^2} = 65.6 \text{ (surface water).}$$

According to the calculation results, the risk of contamination of groundwater with spiromesifen in the studied soil and climatic conditions by the integral vector R was average. An integral index of hazard of pesticide contaminated water consumption (IIHPCWC)

Table 1: Spiromesifen persistency in soil in different soil and climatic conditions.

Data source	Soil type	τ_{50} , Days	τ_{90} , Days	Hazard Class		
				State Standard	IUPAC	
EU ¹³	LC	podzolic	4.1	13.8	4	3
	FC	chestnut	2.1	–	4	3
USA ¹³ (different soil types)	1	podzolic	4.6	15.4	4	3
	2	red-chestnut	2.1	6.9	4	3
	3	brown forest	6.4	21.1	4	3
	4	chernozem	4.5	15.0	4	3
PPDB ¹³		sandy, chernozem, podzolic	1.9 – 10.6	6.3 – 56.7	4	3
PubChem ¹⁴		sod-carbonate	6 – 21	2.6 – 17.9	4* – 3*	3
FAO ¹⁵	LC	brown forest	2.6 – 17.9	–	4* – 3*	3
	FC	brown forest	5.0	–	4	3
Own research (average value)		chernozem, chestnut, sod-podzolic, gray forest	7.8	28.9	4	3

Notes: LC – laboratory conditions; FC – field conditions; τ_{50} half-life of the substance; τ_{90} – period of destruction of 90 % of the substance; «*» – class on the minimum value / class on the maximum value.

Table 2: Spiromesifen mobility indices in soil and climatic conditions of Ukraine.

Evaluation Criteria	LEACH _{mod} , c.u.	GUS	K _{oc} , c.u.	S _w , mg/l	τ_{50} in the Soil, Days
The magnitude of the index	3.3×10^{-5}	-0.92	30900	0.13	7.8
Score in points	1	30	–	–	–
Hazard class by ⁵	3	6 3a ⁷	5	–	4

Notes: LEACH_{mod} – leaching index; c.u. – conventional units; GUS – ground ubiquity score; K_{oc} – sorption constant of organic carbon; S_w – solubility of the substance in water; τ_{50} – substance half-life.

Table 3: Assessment of the spiromesifen migration capacity in surface and groundwater.

Indicators of Danger	PPDB ¹³	Own Research	Score in Points	Level of Hazard	
				Level	Class ⁷
GUS, c.u.	-0.16	-0.92	30/30	low	6/6
τ_{50} in groundwater, days	44.7	7.8	50/30	medium/low	2/4
τ_{50} in surface waters (water-sediment system), days	5.95	> 2	30/30	low	4/4

Notes: GUS – ground ubiquity score; c.u. – conventional units; τ_{50} – the period of destruction of 50 % of the substance.

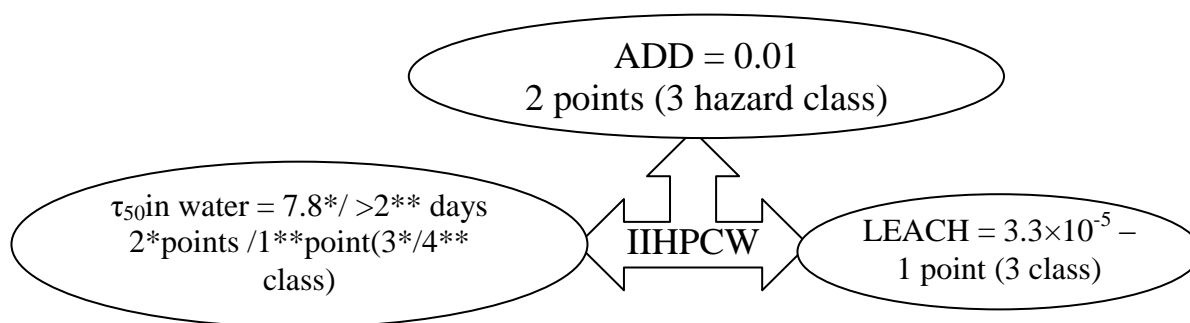
was calculated based on LEACH_{mod}, τ_{50} in water (for groundwater – due to hydrolysis at pH = 7, for surface water – in the aqueous phase of the water-sediment system) and acceptable daily dose (ADD):¹²

IHPCWC = 1 + 2 (1) + 2 = 5 (4) points. It was evaluated by a 4-point gradation.¹² According to this method, spiromesifen was a moderately hazardous substance for humans due to groundwater contamination

Table 4: Assessment of cumulative properties and toxicity of spiromesifen.

Sources		Lim _{ch} , mg/kg	LD ₅₀ , mg/kg	Z _{biol.ef}	Hazard Level, Points
PPDB ¹³		14.2	2000	140	medium (50)
Own research	Males	6.5	2000	307	medium (50)
	Females	19.3		104	medium(50)

Notes: Lim_{ch} –threshold of chronic effect after oral treatment; LD₅₀ –amount of material, given by oral route at once, which causes the death of 50 % of test animals.

**Fig. 1: Assessment of integral index of hazard of pesticide contaminated water consumption.**

Notes: "*" – half-life in groundwater; "***" – half-life in surface waters; ADD – acceptable daily dose for humans; IIHPCW – integral index of hazard of pesticide contaminated water consumption; LEACH – leaching index; τ_{50} – half-life of the substance.

(class 3) and low-risk (class 4) due to surface water contamination.

DISCUSSION

Degradation of pesticides in soil depends on many factors: soil and climatic conditions, mechanical composition of soil, pH, humus content, humidity and temperature, physicochemical properties of pesticides, consumption rates and method of application of the formulation.³ The main factor that determines the rate of destruction and intensity of pesticide migration is the sorption-desorption equilibrium in the pesticide-soil system, according which spiromesifen is low mobile.

However, the potential danger increases with long-term persistence of the substance in the soil, its high solubility in water and significant hydrolytic stability, so the prognosis of soil contamination only for K_{oc} cannot be final. According to main surface and groundwater leaching indices spiromesifen has a low risk of potential contamination of such water bodies.

Obtained GUS and LEACH indices evaluation almost coincide with the data obtained in other soil and climatic conditions and for other types of pesticides.¹⁶ The potential risk of contaminated water consumption according to IIHPCW (Fig. 1) is one of the lowest among other pesticides.¹⁷

CONCLUSION

It was established that spiromesifen by persistency in soil and climatic conditions of Steppe, Forest-Steppe, Polissya belongs to low-stability pesticides, and characterized by low mobility in soil. Spiromesifen had a low possibility of leaching into groundwater and a low risk of groundwater and surface water contamination. It was a moderately hazardous substance for humans due to groundwater contamination (class 3) and low-risk (class 4) due to surface water contamination by the integral index of hazard of pesticide contaminated water consumption.

Based on the above results, it is possible to widely introduce a new insecticidal compound spiromesifen in agricultural practice. At the same time, we recommend strictly follow the recommended hygienic standards and regulations when using pesticides based on this active substance.

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