ORIGINAL ARTICLE

COMPARATIVE HYGIENIC ASSESSMENT OF PESTICIDES BEHAVIOR IN SOIL IN INTENSIVE GRAIN FARMING TECHNOLOGIES

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ABSTRACT

The aim: Was the comparative hygienic evaluation of the pesticide behavior in the soil after application on cereals.

Material and methods: Methods of full-scale in-field hygienic experiment, high-performance liquid (HPLC), gas-liquid (GLC), thin-layer chromatography, statistical, bibliography were used in the research.

Results: Data on the detailed conditions and land parcels treated with studied pesticide formulation and its a.i. are highlighted in the article. The actual levels of the different classes a.i. content in soil and its dynamics were determined, based on which the dissipation rate constants (K) were calculated, as well as quantitative parameters of stability (τ_{50}, τ_{95}, τ_{99}).

Conclusions: Azoxystrobin, benzovindiflupyr, epoxiconazole, propiconazole, prochloraz, cyproconazole can be classified as of low hazardous substances, and trinexapac-ethyl, kresoxim-methyl, picoxystrobin, and tebuconazole are considered to be moderately hazardous. Among all pesticides studied, tebuconazole is the longest persists in the soil; epoxiconazole and propiconazole are most likely to disappear from the soil. Calculated values of half-lives of the studied substances in the agro-climatic conditions of Ukraine are slightly different from the results of in-field experiments that were conducted in other countries, namely: azoxystrobin, epoxiconazole, propiconazole, and cyproconazole disappear from the soil more quickly; the kresoxim-methyl and pinoxaden disappear more slowly. Meanwhile, the persistence of benzovindiflupyr, picoxystrobin, prochloraz, trinexapac-ethyl, and tebuconazole does not differ from the persistence in soils of European countries.

KEY WORDS: soil dynamics, persistence, plant protection, hygiene

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INTRODUCTION

Every year, as a result of increasing both the quantitative use of chemical protection products of plants and their qualitative diversity, the likelihood of pesticidal load on environmental objects and the risk of accumulation of their residues, migration along trophic chains of food increases. [1-3]. For humans, this can lead to direct danger through the contamination of plants and plant products with pesticide residues. The most contaminated object of the biosphere is soil that can be repeatedly contaminated during the season or for many years. Therefore, soil from a sanitary and hygienic point of view is a potential place for the longest and most massive accumulation of plant protection chemicals. Contamination of soil by compounds of different chemical classes can lead to disruption of the life of microorganisms, the processes of recovery and soil formation may also be distorted [4]. It should also be taken into account that after repeated use of pesticides, the composition of microflora capable of biotransforming and decomposing these substances is disturbed. This all leads to a decrease in the target effect of pesticide formulations and the effectiveness of active ingredients (a.i.) in the fight against crop pests falls clearly [5-8]. However, with the same biological activity of the active substances against the target objects, the criteria for their selection should be human safety and environmental safety.

THE AIM

The purpose of the work was the comparative hygienic evaluation of the behavior of active substances of chemical plant protection products in the soil after application on cereals.

MATERIALS AND METHODS

Methods of full-scale in-field hygienic experiment, high-performance liquid (HPLC), gas-liquid (GLC), thin-layer chromatography, statistical, bibliography were used in the research.

Data on studied formulations (F.) #1-9, land parcels types are given in table 1.

Sampling was carried out in accordance with the "Uniform Rules for Sampling of Agricultural Products, Foodstuffs and Environmental Objects to Determine Micro-Quantities of Pesticides".

Cereal crops were treated using a MZU-320 sprayer connected to a UMZ tractor (F. 8), and using an OPSh-2000 sprayer connected to MTZ-82 tractor (F. 1, F. 4, F. 5, F. 6, F. 9, F. 2), Landini-2000 (F. 7), MTZ-80 (F. 3) or using a hinged spray drier mounted on the AeroS-2 trike (F. 1, F. 6).

For a more detailed determination of the behavioral characteristics of a.i. of pesticides in the environment, we conducted full-scale in-field studies in different agro-climatic zones of Ukraine, which are characterized by different types of soils.

Table 1. In-field conditions for the research of studied formulations [9]

Number of land parcel	Location of the site / formulation	Soil type
		Forest-Steppe, Right Bank Province
1.	49°48'17"N 29°46'04"E 2	Chernozems podzolized + Chernozems deep, low humus, leached (Chernic)
2.	49°56'42"N 30°12'40"E 3	Chernozems deep, low humus, leached
3.	49°47'59"N 30°00'04"E 4	Chernozems typical, very goodhumus-accumulating
4.	50°20'24"N 30°25'22"E 9	Gray forest moderately to low humusacumulative + Dark gray podzolized medium humus accumulative
5.	49°36'29''N, 28°05'51''E 5	Chernozems typical moderately high humusacumulative
6.	49°21'07"N 27°21'15"E 1, 6	Dark gray podzolized medium humus accumulative + Chernozems podzolized medium to high humusacumulative
		Forest-Steppe, Left Bank Lowland Province
7.	50°15'33"N, 31°09'31"E 7	Dark gray podzolized medium to low humusacumulative + Chernozems podzolized medium humusacumulative
8.	50°29'59"N 31°14'47"E 8	Meadow and chernozem-meadow surface-saline soils + Light gray podzolic soils + Chernozems podzolized (Gleysols Sodic, Phaeozems Albic)
		Forest-Steppe, West Province
9.	48°37'15"N 25°44'15"E 1, 6	Chernozems podzolized + gray podzolic soils mainly on loessial rocks

RESULTS

Data on the detailed conditions and land parcels treated with studied pesticide formulation and its a.i. are presented in table 1. The actual levels of the different classes a.i. content in soil and its dynamics were determined, based on which the dissipation rate constants (K) were calculated, as well as quantitative parameters of stability (τ_{50}, τ_{95}, τ_{99}). The results of the level of studied a.i. residues determined in the soil are shown in table 2.

Soil samples were collected 3 days after cereal crops treatment by studied formulations.

It should be noted that studied a.i. were not found in all soil control samples (i.e. less than relevant limits of detection (LODs) by appropriate chromatographic methods).

Having analyzed the data obtained in the studies of the level dynamics, it can be stated that a.i. residue concentrations in the studied samples were decreasing gradually.

A.i. behavior patterns in the soil from the experimental land parcels allocated for cereal crops were studied at the stage of treatment with formulations 1-9 by rod spraying method during the vegetative period

On the treatment day, residual amounts of the active ingredients of the F. 6 were determined at 0.11±0.02 mg/kg, 0.06±0.3009 mg/kg and 0.04±0.005 mg/kg levels for propiconazole, benzovindiflupyr, and cyproconazole, respectively. Since the day of treatment, the level of propiconazole in soil was below the TAC (0.2 mg/kg), while the level of cyproconazole passed this value only after 7 days (0.01 mg/kg). At the time of harvest (55 days for spring barley and 60 days for winter wheat and barley), no residual amounts of these active substances were found in the soil. The results of field studies that were obtained in determining the active substances of other pesticides (fungicides, herbicides and plant growth regulators) concentration levels in the soil were analyzed (F. 1, F. 4, F. 5, F. 7, F. 9, F. 2, F. 3, F. 8).

3 days after the treatment of winter wheat and barley crops with F. 1, the concentrations of azoxystrobin and cyproconazole in the soil were 0.025±0.004 mg/kg and <0.01 mg/kg, respectively, which in turn is less than the approved levels of TAC (0.3 mg/kg for azoxystrobin and 0.01 mg/kg – for cyproconazole).

Field studies of the F. 4 behavior in the soil revealed that 3 days after treatment the concentration levels were 0.27±0.06 mg/kg for prochloraz, 0.1±0.05 mg/kg for epoxiconazole, respectively. On the 7th day after treatment, the concentration of prochloraz was 0.18±0.02 mg/kg, epoxiconazole – 0.03±0.01 mg/kg, these values are lower than the established TAC for these a.i. (prochloraz – 0.3 mg/ kg, epoxiconazole – 0.4 mg/kg).

When using F. 5, studies were conducted to determine the residual amounts of kresoxim-methyl and tebuconazole. The concentrations of kresoxim-methyl and tebuconazole

Table 2. Content of a.i. in soil samples after pesticide formulation application on cereal spiked crops

Formulation	Active ingredient	Standard in soil, tentatively allowable concentration (TAC), mg/kg	Content of a.i. in treated soil after …days, mg/kg:	
			3 days	7 days
Rod treatment				
F. 1	azoxystrobin	0,3	0,025±0,004	0,012±0,002
	cyproconazole	0,01	<0,01	<0,01
F. 2	picoxystrobin	0,2	0,12 ± 0,03	0,1 ± 0,03
	cyproconazole	0,01	0,04 ± 0,01	0,04 ± 0,01
F. 3	pinoxaden	0,3	0,11±0,03	<0,1
F. 4	prochloraz	0,3	0,27±0,06	0,18±0,02
	epoxiconazole	0,4	0,1±0,05	0,03±0,01
F. 5	tebuconazole	1,0	0,09±0,01	0,081±0,01
	kresoxim-methyl	0,1	0,056±0,008	<0,05
F. 6	benzovindiflupyr	0,03	0,041±0,008	0,030±0,005
	propiconazole	0,2	0,08±0,01	0,036±0,005
	cyproconazole	0,01	0,015±0,003	<0,01
F. 7	azoxystrobin	0,3	0,026±0,005	<0,01
	tebuconazole	1,0	0,08±0,016	0,072±0,01
F. 8	trinexapac-ethyl	0,6	0,11 ± 0,03	<0,1
F. 9	azoxystrobin	0,3	0,03±0,005	<0,01
	tebuconazole	1,0	0,091±0,018	<0.05
Aerial spraying				
F. 1	azoxystrobin	0,3	0,01±0,002	<0,01
	cyproconazole	0,01	<0,01	<0,01
F. 6	benzovindiflupyr	0,03	0,036±0,005	<0,03
	propiconazole	0,2	0,11±0,01	0,04±0,007
	cyproconazole	0,01	0,011±0,001	<0,01

in soil were determined at 3 and 7 days after treatment. At 3 days the concentration levels of the studied a.i. were below the established TAC: the residual amount of kresoxim-methyl was 0.056±0.008 mg/kg (TAC – 0.1 mg/kg), tebuconazole – 0.09±0.01 mg/kg (TAC – 1.0 mg/kg).

Studies were also conducted to determine the residual amounts of azoxystrobin and tebuconazole (the a.i. of F. 7) in soil samples taken after winter wheat crop treatment. Determining the concentration of these substances, it was found that at 3 days after treatment, the level of azoxystrobin was 0.026±0.005 mg/kg, tebuconazole – 0.08±0.016 mg/kg. At both the third and the seventh day, soil concentrations of azoxystrobin and tebuconazole were lower than the established TAC (0.3 mg/kg and 1.0 mg/kg, respectively).

After the application of the F. 9 preparation on the wheat crops, we determined the levels of a.i. concentration in soil samples picked from the treated area. Examining the concentrations of the substances presented, it was found that at 3 days after treatment the level of azoxystrobin was 0.03±0.005 mg/kg, tebuconazole – 0.091±0.018 mg/kg. At day 7, azoxystrobin and tebuconazole were not determined (TAC for azoxystrobin is 0.3 mg/kg, tebuconazole – 1.0 mg/kg).

After cereal crops treatment with F. 3 herbicide, its active substance pinoxaden was determined in soil samples at the level of 0.11±0.03 mg/kg and <0.1 mg/kg (3 and 7 days, respectively), which in turn is lower TAC (0.3 mg/kg).

On the third day after performed full-scale studies on the use of combined fungicide F. 2 it was found that the concentration of cyproconazole in the soil for both 3 and 7 days was 0.04±0.01 mg/kg, the concentration of pyraclostrobin was determined at 0.12±0.03 mg/kg and 0.1±0.03 mg/kg on days 3 and 7, respectively, which in turn is less than the previously established TAC (0.2 mg/kg). The concentration of cyproconazole at the time of harvest (40 days) was below the limit of determination of the relevant method.

3 days after the application of plant growth regulator F. 2 its active substance trinexepac-ethyl was determined at the level of 0.11±0.03 mg/kg, at day 7 – <0.1 mg/kg, these findings indicate that a.i. were not exceeded soil TAC values (0.6 mg/kg).

We have also further investigated and analyzed the patterns of migration of active substances of the preparations F. 6 and F. 1 (azoxystrobin, benzovindiflupyr, propiconazole, and cyproconazole) in soil samples from the cereal crops area during aerial spraying.

Table 3. The rate of the studied pesticides dissipation/disappearance in the soil

Formulation	Active ingredient	Indices of dissipation/disappearance in soil				
		k^{-1}	τ_{50}	τ_{95}	τ_{99}	τ_{50}*
Rod treatment						
F. 1	azoxystrobin	0,183± 0,001	3,757± 0,020	16,334± 0,088	25,045± 0,135	120,9 – 261,9
	cyproconazole	0,109± 0,037	8,305± 3,121	36,108± 13,571	55,365± 20,809	62,1 – 501,2
F. 2	picoxystrobin	0,032± 0,0022	21,78± 1,543	94,68± 6,708	145,20± 10,29	2,6-37,0
	cyproconazole	0,058± 0,0006	11,90± 0,068	51,74± 0,294	79,33± 0,451	62,1-501,2
F. 3	pinoxaden	0,052± 0,0030	13,07± 0,4881	56,82± 2,122	87,13± 3,254	0,07-1,01
F. 4	prochloraz	0,098± 0,017	7,490± 1,382	32,562± 6,007	49,929± 9,211	1,9 – 73,2
	epoxiconazole	0,287± 0,030	2,464± 0,280	10,714± 1,218	16,428± 1,868	44-226
F. 5	tebuconazole	0,027± 0,002	26,196± 1,772	113,893± 7,705	174,637± 11,815	25,8 – 91,6
	kresoxim-methyl	0,061± 0,019	14,300± 5,146	62,176± 22,375	95,334± 34,307	1 – 3
F. 6	benzovindiflupyr	0,098± 0,001	7,036± 0,079	30,560± 0,344	46,910± 0,527	0,001 – 336**
	propiconazole	0,161± 0,003	4,287± 0,090	18,637± 0,389	28,577± 0,596	15,3 – 96,3
	cyproconazole	0,192± 0,011	3,621± 0,218	15,744± 0,946	24,140± 1,451	62,1 – 501,2
F. 7	azoxystrobin	0,236± 0,028	3,016± 0,375	13,113± 1,631	20,113± 2,496	120,9 – 261,9
	tebuconazole	0,024± 0,009	43,546± 21,838	189,329± 94,948	290,307± 145,585	25,8 – 91,6
F. 8	trinexapac-ethyl	0,047± 0,0002	14,75± 0,04676	64,13±0,2033	98,33±0,3117	6,9-21
F. 9	azoxystrobin	0,122± 0,018	5,957± 1,006	25,898± 4,376	39,710± 6,709	120,9 – 261,9
	tebuconazole	0,034± 0,005	20,973± 2,820	91,188± 12,261	139,821± 18,799	25,8 – 91,6
Aerial spraying						
F. 1	azoxystrobin	0,066± 0,019	12,042± 2,710	52,359± 11,781	80,283± 18,065	120,9 – 261,9
	cyproconazole	0,109± 0,037	8,305± 3,121	36,108± 13,571	55,365± 20,809	62,1 – 501,2
F. 6	benzovindiflupyr	0,069± 0,017	11,416± 3,157	49,636± 13,726	76,108± 21,046	0,001-336**
	propiconazole	0,202± 0,005	3,423± 0,079	14,880± 0,341	22,820± 0,526	15,3 – 96,3
	cyproconazole	0,094± 0,012	7,629± 1,062	33,171± 4,616	50,862± 7,078	62,1 – 501,2

Footnotes: 1. «k-1» – dissipation rate constant (days); 2. «τ50» – time for disappearance of half the chemical (days); 3. «τ95» – time for disappearance of 95% of the chemical (days); 4. «τ99» – time for disappearance of 99% of the chemical (days) 5. «*» – reference data [12-13] 6. «**» – reference data [14].

Starting 3 days after cereal crops treatment with F. 6, the level of propiconazole content in the soil was 0.11±0.01 mg/kg and, accordingly, was lower than the TAC level – 0.2 mg/kg, the content of benzovindiflupyr and cyproconazole was 0.036±0.005 mg/kg and 0.011±0.001 mg/kg, respectively. On day 7, benzovindiflupyr and cyproconazole were determined in the soil below the limit of quantification (0.03 mg/kg and 0.01 mg/kg, respectively), and the value for cyproconazole was lower than the TAC (0.01 mg/kg).

3 days after F. 1 application on winter wheat and barley crops f, the concentrations of azoxystrobin and cyproconazole in the soil were 0.01±0.002 mg/kg and <0.01 mg/kg (below the limit of quantification), respectively. This, in turn, is less than the established TAC levels (for azoxystrobin is 0.3 mg/kg, and cyproconazole – 0.01 mg/kg).

For a more detailed evaluation of the data we obtained, several mathematical analyzes of the degradation processes of the studied a.i. were conducted, using an exponential model using the first-order kinetics equation [9, 10].

The results of the conducted studies to determine the level of residual content of the a.i. in the soil (Table 3) allowed us to calculate the dissipation rate constant (K) and quantitative parameters of substances persistency in environmental objects using the least-squares method: decay periods by 50%, 95 % and 99% (τ_{50}, $\tau_{95,}$ and τ_{99})

DISCUSSION

The value of azoxystrobin τ_{50} in different agro-climatic conditions of Ukraine ranges from 3.03 to 12.04 days, these findings differ from those established in the European region [11, 12]. The half-life of azoxystrobin in parcel site (p.s.) 9 soils is significantly faster compared to a similar process in p.s. 4 and p.s. 6 ($p \leq 0.05$).

During the experiments, it was found that the half-life of kresoxim-methyl in p.s. 5 passes in 14.3±5.15 days. The half-life of another representative of the strobilurins class – picoxystrobin in p.s. 1 was 21.78±1.543 days.

τ_{50} of benzovindiflupyr for p.s. 6 and p.s. 9 soils is 7.04 and 11.42 days, respectively, and does not have significant differences ($p \geq 0.05$). Benzovindiflupyr biodegradation processes in Ukraine's agro-climatic conditions are faster than in the European region [13, 15].

Studying the features of the degradation processes of triazoles (epoxiconazole, propiconazole, tebuconazole, and cyproconazole) in the soil, it was found that the half-life of the substances presented is: for epoxiconazole τ_{50} – 2.47±0.28 days; for propiconazole τ_{50} – 3.85±0.19 days; for cyproconazole τ_{50} – 7.95±1.04 days; for tebuconazole τ_{50} – 30.19±7.15 days. Propiconazole half-lives (τ_{50}) for p.s. 6 and p.s. 9 areas are 3.62±0.22 and 7.63±1.06 days, respectively. Propiconazole was found to decompose significantly faster in p.s. 6 ($p \leq 0,05$).

Determining the degradation processes for the active substance prochloraz under in-field conditions, we obtained the following results: 50% decay in p.s. 3 soils occurs at 7.49±1.38 days.

Also during the experiments, it was found that the half-life of pinoxaden in p.s. 3 soils is 13.07±0.49 days. And the half-life of trinexapac-ethyl in p.s. 8 soils was 14.75±0.047 days.

The differences in the degradation rates of the studied active substances, which were calculated for individual areas, can be associated with different types of soils and climate and weather conditions, it should be noted that the rate of neutralization of active chemical compounds in the soil depends on its pH value, atmospheric parameters of air, namely humidity and temperature, solar activity (the intensity of ultraviolet radiation), as well as the amount of active substance applied [14-16]. According to the Hygienic Classification of Pesticides by the Degree of Hazard currently in force in Ukraine, by the soil persistence in the agro-climatic conditions of Ukraine azoxystrobin, benzovindiflupyr, epoxiconazole, propiconazole, prochloraz, cyproconazole can be classified as of low hazardous substances (grade IV), and trinexapac-ethyl, kresoxim-methyl, picoxystrobin, and tebuconazole are considered to be moderately hazardous (grade III). Among all pesticides studied, tebuconazole is the longest persists in the soil; epoxiconazole and propiconazole are most likely to disappear from the soil.

CONCLUSIONS

It should be noted that our calculated values of half-lives of the studied substances in the agro-climatic conditions of Ukraine are slightly different from the results of in-field experiments that were conducted in other countries, namely: azoxystrobin, epoxiconazole, propiconazole, and cyproconazole disappear from the soil more quickly; the kresoxim-methyl and pinoxaden disappear more slowly [12].

Meanwhile, the persistence of benzovindiflupyr, picoxystrobin, prochloraz, trinexapac-ethyl, and tebuconazole in the agro-climatic conditions of Ukraine does not differ from the persistence in soils of European countries [11].

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The Authors declare no conflict of interest.

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