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PREDICTION OF HAZARD FOR SOIL AND GROUNDWATER CONTAMINATION WITH DIFFERENT CLASSES OF PESTICIDES INTENDED TO PROTECT OIL CROPS IN SOIL AND CLIMATIC CONDITIONS OF UKRAINE

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ABSTRACT. *Depositing in soil, pesticides are able to enter ground- and surface water with their subsequent contamination.* ***The study aimed*** *to perform hygienic assessment of soil and groundwater pollution with different chemical classes of pesticides used for chemical protection of oil crops.*

Materials and Methods. *Field survey was carried out to study migration dynamics of pesticides residual amounts in soil, which were applied by above-ground and aerial methods. Half-life period (DT_{50}) was measured for the studied active substances (a.s.) in soil using mathematical modelling; migration probability was assessed into groundwater using the organic carbon sorption constant (Kos), leaching potential index or Groundwater ubiquity score (GUS) and potential contamination index for ground- and river water (LEACH). Integral vector of the groundwater contamination hazard (R) and integral groundwater contamination index for pesticides (IGCHI) were used to assess the possible their negative impact on human health.*

Results. *It was found that all studied a.s. were rated to moderately (III class) or low (IV class) hazardous pesticides by their stability in soil of Ukraine (except pymetrozine, which was rated to hazardous (II class) pesticide by its maximum DT_{50}). Strobilurin fungicides had the least migration probability into groundwater while nicosulfuron and dicamba herbicides – the highest one. Picoxystrobin and diflufenzopyr had the average hazard level by integral vector R; they were hazardous and moderately hazardous by IGCHI. Dicamba, difenoconazole and pymetrozine had the high hazard level by integral vector R; they were extra- and highly hazardous by IGCHI. Hazard assessment for the ground- and surface water contamination due to pesticide migration from soil was not the same by different procedures, they complemented each other. To protect oil-bearing crops, preference should be given to pesticides with the least contamination hazard for soil, groundwater and surface watercourses, namely: picoxystrobin, diflufenzopyr and pyraclostrobin.*

Key words: *fungicides, herbicides, insecticides, soil, underwater, hazard assessment.*

Soil and climatic conditions in most Ukrainian regions are suitable for cultivation strategically important agricultural crops, including oil ones. Ensuring efficient protection of crops from pests, diseases and infestation by using insecticides, fungicides and herbicides is a pre-condition for successful agriculture. In addition to useful maintaining the crop, herbicides constitute a potential hazard to the environment and human health. Soil is the main pesticide depot in the environment; therefore, the threat exists of penetration of chemical crop protection products (CCPP) from soil into groundwater, first of all, to subsoil and surface water and its subsequent pollution [1]. It is worth noting that almost 70 % of rural population in Ukraine live without centralized water supply and consume water from wells, where the contamination probability with pesticides may be the highest (as compared to confined water, in particular, artesian one).

That is why the **objective** of our study was hygienic assessment of the contamination hazard for soil and groundwater with modern pesticides rated to different chemical classes used in chemical protection of oil crops.

Materials and Methods. The following pesticides were studied within this research: strobilurine (azoxysrobin, pyraclostrobin, picoxystrobin) and triazole (difenoconazole) fungicides, pymetrozine insecticide (pyridinic azomethine class), nicosulfuron (sulphonyl urea with pyrimidine heterocycles), dicamba (derivative of benzoic acid) and diflufenzopyr (semicarbazone) herbicides. Formulations contained the above-mentioned active components (a.c.) were recommended for chemical protection of sunflower, corn and rape (Table 1).

Field hygienic experiments were carried out in Polissiya (Kyiv, Khmelnytskyi regions) and Forest-Steppe (Cherkassy, Chernivtsi regions) zones of Ukraine according to [2] and intended to assess the dynamics of residual amounts of the studied pesticides in soil after their above-ground and aerial treatment.

We calculated half-file periods (DT_{50}) of the studied substances in soil, which allowed to

Table 1

Application conditions of the studied formulations by their active substances

Formulation	**Active substance, concentration in the formulation**	**Application region (climatic zone), consumption rate of the formulation, maximum amount of treatments *(crop)***	
		Above-surface treatment	**Aerial treatment**
Kelvin Plus, granules dispersed in water	Dicamba, 424 g/kg; Diflufenzopyr, 170 g/kg; Nicosulfuron 106 g/kg	Kyiv Region (Polissiya), 0.4 kg/ha, single *(corn)*	—
Plenum 50 WG, granules dispersed in water	Pymetrozine, 50 g/l	Kyiv Region (Polissiya), 0.25 kg/ha, single *(rape)*	—
Acanto, suspension concentrate	Picoxystrobin, 250 g/l	Kyiv Region (Polissiya), 1.0 l/ha, twice *(corn, sunflower)*	Cherkassy Region (Forest-Steppe), 1,0 л/га, одноразово *(corn, sunflower)*
Retengo, emulsified concentrate	Pyraclostrobin, 200 g/l	—	Cherkassy Region (Forest-Steppe), *corn* - 0,5 л/га; *sunflower* –0,75 л/га, одноразово
Amistar Gold 250 SC, suspension concentrate	azoxysrobin, 125 g/l; Difenoconazole, 125 g/l	Khmelnytskyi Region (Polissiya), 1.0 l/ha, twice *(sunflower)*	Chernivtsi Region (Forest-Steppe), 1,0 л/га, двоpазово *(sunflower)*

predict their persistence using mathematical modeling that provided computational replication of the pesticide decomposition processes based on actual data.

Hazard class of the studied substances by their stability in soil was defined according to State Sanitary Standards and Rules (DSanPin) 8.8.1.002-98 (I class – highly persistent pesticides (DT_{50} exceeds 60 days), II – persistent (31 days to 60 days), III – moderately persistent (11 days to 30 days) and IV – low persistent (less than 11 days)) and by the IUPAC international classification (I class – highly persistent (DT_{50} exceeds 100 days), II class – moderately persistent (30 days to 100 days), III class – low persistent (less than 30 days)) [3, 4].

We assessed potential risk of the studied pesticides for the environment using the procedure worked out by N.N. Melnikov [5] by calculating environmental toxicity (ecotox) by the formula:

$$E = \frac{P \times N}{LD_{50}}$$

where: E — is ecotoxicological hazard, arbitrary units;

P — is the substance half-life, weeks;

LD_{50} — is the substance median lethal dose at its ingestion intake by white rats, mg/kg.

Ecotox allows to compare environmental toxicity of a studied substance and dichlorodiphenyltrichloroethane (DDT) and to estimate relative hazard of soil contamination with this substance since the DDT ecotoxicological hazard is taken as an ecotox arbitrary unit (at consumption rate 1 kg/ha, persistence 312 weeks and LD_{50} – 300 mg/kg).

Migration probability for the studied a.s. in groundwater in different soil and climatic conditions of Ukraine was predicted by the following indicators: organic carbon sorption constant (K_{oc}), potential leaching index (GUS – Groundwater Ubiquity Score) and index of potential contamination of groundwater and river water (LEACH).

To estimate migration capability by K_{oc} constant, we used SSLRC (Soil Survey and land research centre) International classification, which divides all substances into 5 classes: I – very mobile (K_{oc} is less than 15 ml/g), II – mobile (15 ml/g to 74 ml/g), III – moderately mobile (75 ml/g to 499 ml/g), IV – slightly mobile (500 ml/g to 4,000 ml/g), V – non-mobile (more than 4000 ml/g) [6].

GUS was calculated by the formula [7]:

$$GUS = \lg DT_{50} \times (4 - \lg Koc)$$

where: DT_{50} — is the substance half-life period in soil, day;

K_{oc} — is the organic carbon sorption constant, ml/g.

If the GUS value exceeds 2.8, the pesticide, probably, is leached into groundwater; if it is less than 1.8, the pesticide, probably, is not leached into groundwater; its leaching probability is minor at GUS value 1.8 to 2.8. If GUS > 4.0, leaching probability is considered as very high (I class), 3.0 to 4.0 – high (II), 2.0 to 3.0 – moderate (III), 1.0 to 2.0 – low (IV), 0.1 to 1.0 – very low (V), less than 0.1 – extremely low [7].

LEACH was calculated using the formula [8]:

$$LEACH_{\text{mod.}} = \frac{S_w \times DT_{50\,field}}{K_{oc}}$$

where: S_w — is the substance solubility in water, mg/l;

$DT_{50field}$ — is the substance half-life period in soil in natural conditions, day;

K_{oc} — is the organic carbon sorption constant.

If the LEACH value exceeds 2.0, contamination risk is considered as high for surface and ground water (I class), 1.1 to 2.0 – moderate (II) and 0.0 to 1.0 – low (III).

GUS and LEACH indicators were calculated using literature data on sorption factors K_{oc} and solubility in water [9]. We used the own field survey data in soil and climatic conditions of Ukraine when calculating half-life periods of the studied substances in the soil.

Since the all above indicators allow to estimate only the penetration possibility into groundwater for the studied pesticides, we used integral vector of the groundwater contamination hazard (R) worked out by S.G. Sergeev et al. [10] and integral groundwater contamination index for pesticides (IGCHI) according to the prediction method for the pesticide negative impact on the population due to their intake with water [11], which was created with our participation. Both indicators integrated three parameters: ability of the substance to migrate from the soil to groundwater, duration of water contamination by its half-life due to hydrolysis (τ_{50}) and the substance toxicity and cumulative effect. At the same time, GUS values were used to assess the possibility of the substance migration from the soil to groundwater by the procedure [10] and LEACH indicator by the procedure [11], which defined the contamination possibility not only ground- but also surface water (in particular, rivers) and considered the substance solubility in water in addition to Koc and the substance half-life in soil. A biological effect zone ($Z_{biol.ef.}$) is used to estimate the pesticide toxicity and cumulative effect according to the procedure [10], and the permissible day dose (PDD) by the procedure [11].

Biological effect area ($Z_{biol.ef.}$) was calculated using the equation:

$$Z_{biol.ef.} = LD_{50} / Lim_{ch},$$

where: LD_{50} — is median lethal dose of a pesticide at its single administration in rat ventricle, mg/kg;

Lim_{ch} is the chronic effect threshold at oral administration in rats, mg/kg.

Values of GUS, τ_{50} in water and in a biological effect zone were assessed according to [10] using a scale containing four hazard levels: low (30 points), moderate (50), high (80) and extremely high (100).

Integral hazard vector (R) was calculated using the formula:

$$R = \sqrt{x^2 + y^2 + z^2}\ ,$$

where x, y, z were point assessment of the potential leaching index, half-life due to hydrolysis in water and a biological effect zone, correspondingly.

To calculate an integral groundwater contamination index for pesticides (IGCHI), we assessed LEACH and τ_{50} values in water and DDD in points using the scale that provided 4 grading levels [11] and used the formula:

$$IGCHI = LEACH^* + \tau_{50}^* + DDD^*,$$

where: LEACH*, τ_{50}*, DDD* are point assessment of LEACH index, τ_{50} in water (due to hydrolysis at pH=7 for groundwater and in aqueous phase of the "water-sediment" system for surface water) and DDD, correspondingly.

At IGCHI value 3 to 4 points, the substance was considered as low-hazardous for humans during its migration within the system "soil – water" (4 class), 5 to 6 points – moderately hazardous (3 class), 7 to 8 points – hazardous (2 class), 9 to 10 points – highly hazardous (1B class), 11 to 12 points – extremely hazardous (1A class).

Results and Discussion. Mathematic modeling of decontamination processes for the studied substances in Ukrainian natural conditions has revealed that diflufenzopyr had the least half-life period (3.4±0.5 days) in soil (Table 2). Difenoconazole (DT_{50} 29.1±5.6 days) and pymetrozine (27.2±3.3 days) had the highest stability among the studied a.s. According to the Ukrainian pesticide classification by their hazard level [3] based on the average DT_{50} values in Ukrainian soils, the studied substances were rated to moderately (III class) or low- (IV class) stable pesticides (correspondingly, to moderate or low hazardous). At the same time, azoxysrobin, difenoconazole and pymetrozine were stable in particular soil and climatic conditions by the DT_{50} maximum values (hazardous – II class). According to IUPAC classification [4], azoxysrobin, difenoconazole and pymetrozine were moderately stable (II class) substances, other pesticides were low-stable (III class).

Results of the field survey performed in soil and climatic conditions of Ukraine concerning persistence of pyraclostrobin, picoxystrobin, nicosulfuron, dicamba, diflufenzopyr and pymetrozine in soil matched the data obtained by other authors in European countries. Concerning azoxysrobin, this substance was the least stable in Ukraine (Table 2).

To estimate potential application risk of the studied pesticides for above-surface ecosystems, their ecotoxicological hazard (ecotox) was calculated using our own research results. We have found out that ecotox value in soil and climatic conditions of Ukraine varied with in 8.55×10^{-6} (diflufenzopyr) to 5.19×10^{-4} (difenoconazole); i.e., ecotoxicological hazard of the studied pesticides was lower by 4 to 6 orders of magnitude for biocenoses than DDT (Table 2).

Sorption-desorption equilibrium within the pesticide-soil system is among prevailing factors that define detoxication speed and migration intensity for CCPP. The studied substances were adsorbed by the soil in a different way. By average values of sorption constant K_{oc} (Table 3), dicamba was rated to very mobile (I class), nicosulfuron – to mobile (II class), azoxysrobin and diflufenzopyr – to moderately mobile (III class), picoxystrobin, difenoconazole and pymetrozine – to low-mobile (IV class) pesticides, pyraclostrobin – to immobile ones (V).

At the same time, prediction of the groundwater contamination using only K_{oc} cannot be final since potential hazard increases due to long persistence of a substance in the soil, its high solubility in water and significant hydrolytic stability. That's why the probability of groundwater and surface water contamination with the studied a.s. was estimated by GUS and LEACH.

The high leaching probability to groundwater was established (Table 3) only for nicosulfuron in soil and climatic conditions of Ukraine (average GUS value was 3.06, maximum – 3.97, II class). According to average GUS values, leaching probability was low for azoxysrobin, picoxystrobin, dicamba, diflufenzopyr and pymetrozine – IV class; very low for difenoconazole (V class), extremely low for pyraclostrobin (VI class). At the worst conditions, leaching probability for azoxysrobin, difenoconazole, dicamba and pymetrozine was moderate (III class).

The results we obtained regarding the probability of groundwater pollution with the studied pesticides either agreed with their assessment made by other experts (nicosulfuron, picoxystrobin) or indicated less risk of groundwater contamination in soil and climatic conditions of Ukraine (diflufenzopyr) (Table. 3). The exception was provided by pymetrozine,which featured the low to moderate (III–IV class) leaching probability in soil and climatic conditions of Ukraine rather than very low (V class) one, difenoconazole and

Table 2

Persistence in the soil and ecotoxicological hazard of the studied pesticides

Pesticide class	Active substance, treatment mode *	DT$_{50}$^{1}, days			Classification		DT$_{50}$^{2}, days	Consumption rate (N), kg/ha	DL$_{50}$, mg/kg	Ecotoxicological hazard	
		M±m	Max.	M±m	DSanPin	IUPAC	M (min–max)			Ecotox** (E), a.u.	Rank
					Average/ max.	Average/ max.					
Strobilurine fungicides	Azoxysrobin, I II	25.7±1.7 19.0±6.7	28.8 31.9	22.4±3.4	III/III III/II	III/III III/II	180.7 (120.9-261.9)	0.125	5000	1.03×10^{-4} 1.14×10^{-4}	VII
	Pyraclostrobin, II	8.3±1.2	10.5	8.3±1.2	IV/IV	III/III	32 (8-55)	0.15	5000	4.5×10^{-5}	IV
	Picoxystrobin, I II	8.8±0.7 9.4±1.8	10.0 12.4	9.1±0.9	IV/IV IV/III	III/III III/III	19.3 (2.6-37.0)	0.25	5000	7.14×10^{-5} 8.86×10^{-5}	V
Sulphonyl urea	Nicosulfuron, I	13.9±2.6	19.0	13.9±2.6	III/III	III/III	19.3 (8.9-63.3)	0.04	5000	2.17×10^{-5}	III
Triazoles	Difenoconazole, I II	38.5±2.1 19.7±8.1	42.2 35.9	29.1±5.6	II/II III/II	II/II III/II	85 (20-265)	0.125	1453	5.19×10^{-4} 4.41×10^{-4}	VIII
Benzoic acid derivatives	Dicamba, I	4.3±0.9	5.8	4.3±0.9	IV/IV	III/III	3.9 (3.2-4.9)	0.1696	1581	8.89×10^{-5}	VI
Semicarbazones	Diflufenzopyr, I	3.4±0.5	4.4	3.4±0.5	IV/IV	III/III	4.5 (3–6)	0.0680	5000	8.55×10^{-6}	I
Pyridinic azomethines	Pymetrozine, I	27.2±3.3	32.0	27.2±3.3	III/II	III/II	22.6 (3.81-183)	0.0125	5820	9.82×10^{-6}	II

Notes: 1. DT$_{50}$^{1} – own study results; 2. DT$_{50}$^{2} – research data in EU countries [9]; 3. * I – boom treatment; II – aerial treatment; 4. ** Exotox was calculated based on the DT501 maximum value.

Table 3

Mobility of the studied pesticides in the soil

Pesticide class	Active substance	DT_{50}^1, days		K_{oc}^2, ml/g			S_w^2, mg/l	GUS^1			GUS^2		$LEACH^1$		
				Value		Rank average /min.		Value		Rank average / max.			Value		Rank
		Average	Max.	Average	Min.			Average	Max.		Value	Rank	Average	Max.	
Strobilurine fungicides	Azoxysrobin I II M±m	25.7 19.0 22.4	28.8 31.9 31.9	423	207	III/III	6.7	1.93 1.75 1.85	2.45 2.52 2.52	IV/III IV/III IV/III	2.65	III	0.41 0.30 0.35	0.93 1.03 1.03	III
	Pyraclostrobin	8.3	10.5	9315	4240	V/V	1.9	0.03	0.38	VI/V	0.06	VI	0.002	0.005	III
	Picoxystrobin I II M±m	8.8 9.4 9.1	10.0 12.4 12.4	898	750	IV/IV	3.1	0.99 1.02 1.01	1.12 1.22 1.22	V/IV IV/IV IV/IV	1.45	IV	0.03 0.03 0.03	0.04 0.05 0.05	III
Sulphonyl urea	Nicosulfuron	13.9	19.0	21	7.9	II/I	7500	3.06	3.97	II/II	3.25	II	4964	18037	I
Triazoles	Difenoconazole I II M±m	38.5 19.7 29.1	42.2 35.9 42.2	3760	400	IV/III	15.0	0.67 0.54 0.61	2.28 2.18 2.28	V/III V/III V/III	0.90	V	0.15 0.08 0.12	1.58 1.35 1.58	III/II
Benzoic acid derivatives	Dicamba	4.3	5.8	12.36	3.45	I/I	250000	1.84	2.64	IV/III	1.75	IV	86974	420289	I
Semicarbazones	Diflufenzopyr	3.4	4.4	87	18	III/II	5850	1.10	1.76	IV/IV	2.36	III	229	1430	I
Pyridinic azomethines	Pymetrozine	27.2	32.0	1049	246	IV/III	270	1.41	2.42	IV/III	0.65	V	7	35	I

Notes: 1 – own study results; 2 – data given in [9].

dicamba, which had a moderate (III class) but not extremely-low and low leaching probability, respectively, in aggravated conditions.

When assessing potential leaching by LEACH, the following results were obtained: nicosulfuron, dicamba, diflufenzopyr and pymetrozine featured the high leaching risk to ground- and surface water (I class). This was due primarily to high water solubility (Sw) of the studied substances (Table. 3). Contamination risk for other a.s. – azoxysrobin, pyraclostrobin, picoxystrobin and difenoconazole – was low (III class) due to their low solubility in water as compared with the above pesticides.

Thus, strobilurine fungicides have the least migration probability to groundwater at soil and climatic conditions of Ukraine among the studied pesticides. In particular, pyraclostrobin and picoxystrobin featured low mobility by K_{oc}, the low leaching probability into groundwater by GUS and the low contamination risk for ground- and surface water by LEACH. Azoxysrobin was moderately mobile, with low/moderate leaching capability and low contamination risk for ground- and surface water by K_{oc}, GUS and LEACH, correspondingly. Nicosulfuron and dicamba featured the highest migration within the “soil – water” system; they were very mobile by K_{oc} and had the high contamination risk for ground- and surface water by LEACH. Besides, nicosufluron had also the high leaching probability by GUS. Our data regarding evaluation of migration capability for azoxysrobin, pyraclostrobin, nicosufluron and difenoconazole agreed with results of the study carried out during other vegetation seasons when using other formulations that protected other agricultural crops [12, 13].

It should be emphasized that all 3 criteria used by us allowed to assess the risk of pesticide penetration in groundwater; however, none of them answered the question how was it hazardous for human health. That’s why integral hazard vector (R) [10] and integral water contamination index for pesticides (IGCHI) [11] were calculated At the same time, based on aggravation principle (one of key principles of hygienic rating and assessment of potentially hazardous environmental factors), maximum values of GUS and LEACH were used to calculate R and IGCHI, which had been obtained during the previous study phase for extreme soil and climatic conditions of Ukraine, where the studied substances had demonstrated the highest persistence (maximum DT_{50} values) at the least sorption capability (minimum K_{oc} values).

It was found that, according to [9], all studied pesticides except for diflufenzopyr and picoxystrobin were hydrolytically stable; they did not decompose in sterile buffer solutions with pH 7 at 20 єC during 30 days (Table 4). By their hydrolytic stability, hazard level of all studied pesticides was high [10] except for diflufenzopyr and picoxystrobin.

According to [10], hazard level was low for picoxystrobin, pyraclostrobin and diflufenzopyr, very high for nicosulfuron and moderate for azoxysrobin, difenoconazole, dicamba and pymetrozine (Table 4).

The studied pesticides were low-toxic at single penetration into ventricle and low-hazardous by LD_{50} at oral administration (Table 2) according to the pesticide hygienic classification by hazard level (DSanPin 8.8.1.002-98). At the same time, pyraclostrobin and pymetrozine were highly hazardous by the biological effect zone, azoxysrobin, picoxystrobin and diflufenzopyr – moderately hazardous, and only nicosulfuron, difenoconazole and dicamba – low hazardous (Table 4).

Integral hazard vector (R) of the studied pesticides (Table 4) decreased in the series: nicosulfuron → pymetrozine → pyraclostrobin → azoxysrobin → difenoconazole, dicamba → picoxystrobin, diflufenzopyr; and according to the assessment scale proposed in [10], it indicated the high-hazard level (except for picoxystrobin and diflufenzopyr, which was moderate for them) for the health of population lived in the areas with potential groundwater contamination due to the pesticide vertical migration from soil.

Integral hazard indicator (IGCHI) of the groundwater contamination with the studied pesticides (Table 4) decreased in the series: difenoconazole, dicamba, pymetrozine (extremely hazardous) → azoxysrobin, nicosulfuron (highly hazardous) → diflufenzopyr, picoxystrobin (hazardous) → pyraclostrobin (moderately hazardous) [11]. IGCHI was relatively low at contamination of surface watercourses with the studied pesticides as compared with ground water pollution since they disappeared from aqueous phase of the “water – sediment” faster than decomposed due to hydrolysis in buffer solution with pH=7. IGCHI decreased

Table 4

Assessment of the hazard to humans caused by contamination of ground- and surface water due to pesticide migration from the soil

Substance	GUS**		LEACH***		τ_{50} in water*, days				$Z_{biol.ef.}$**		DDD***, mg/kg		Integral hazard vector		IGCHI groundwater / surface water	
	GUS	Score, points	LEACH	Score, points	$\tau_{50}{}^1$	$\tau_{50}{}^2$	Score, points		$Z_{biol.ef}$	Score, points	DDD	Score, points	R	Hazard level	Score, points	Rank
							**	*** 1/2								
Azoxysrobin	2.52	50	1.03	4	> 30	6.1	80	4/2	250	50	0.03	1	106.8	high	9/7	1B/2
Pyraclostrobin	0.38	30	0.005	1	> 30	2.0	80	4/1	1,667	80	0.03	1	117.0	high	6/3	3/4
Picoxystrobin	1.22	30	0.05	2	24	7.5	30	3/2	410	50	0.01	2	65.6	moderate	7/6	2/3
Nicosulfuron	3.97	100	18,037	4	> 30	65	80	4/4	34	30	2.0	1	131.5	high	9/9	1B/1B
Difenoconazole	2.28	50	1.58	4	> 30	3.0	80	4/1	40	30	0.002	4	99.0	high	12/9	1A/1B
Dicamba	2.64	50	420,289	4	> 30	40	80	4/4	63	30	0.004	3	99.0	high	11/11	1A/1A
Diflufenzopyr	1.76	30	1,430	4	24	-	30	3/-	192	50	0.04	1	65.6	moderate	8/-	2/-
Pymetrozine	2.42	50	35	4	> 30	6.0	80	4/2	1,572	80	0.003	3	123.7	high	11/9	1A/1B

Notes: 1. * – parameter values were given according to [9]; 2. ** – assessment was made according to [10]; 3. *** - assessment was made according to [11]; 4. 1 – hydrolysis at pH 7 (migration into groundwater); 5. 2 – aqueous phase of the "water–sediment" system (migration into surface watercourses).

in the series when penetrating the studied pesticides into surface water: dicamba (extremely hazardous) → difenoconazole, nicosulfuron, pymetrozine (highly hazardous) → azo-xysrobin (hazardous) → picoxystrobin (moderately hazardous) → pyraclostrobin (low hazardous). Our research data concerning assessment of integral hazard level (IGCHI) at azoxysrobin and pyraclostrobin correlated well with the data of previous studies [12].

Comparative analysis of the results obtained using two procedures for integrated assessment of the hazard to public health caused by contamination of ground- and surface water due to pesticide migration from soil showed that picoxystrobin and diflufenzopyr were the least hazardous among the studied pesticides while dicamba, difenoconazole and pymetrozine were the most hazardous. At the same time, estimates by both procedures were not always unanimous. Thus, the hazard level to the population due to groundwater contamination with pyraclostrobin was moderately high by combined vector R and moderately hazardous in terms of I IGCHI during groundwater polluting and low hazardous when polluting surface watercourses. In addition, none of the procedures did not include consumption rate and multiplicity of pesticide application, did not ensure measurement of possible pesticide concentrations in groundwater and surface water. Therefore, they did not allow to predict and evaluate possible daily entry of a pesticide into a human body in case of the water source contamination.

Conclusions

1. It was found that all studied substances were rated to moderately (III class) or low (IV class) hazardous pesticides by their stability in soils of Ukraine (except pymetrozine, which was rated to hazardous (II class) pesticides by its maximum DT50). Pymetrozine, which was attributed to pyridinic azomethines, persisted the longest in the soil among the studied pesticides; diflufenzopyr attributred to semicarbazones disappeared from the soil the quickest.

2. It was defined that ecotoxicological hazard of the studied pesticides for above-surface biocenoses in Ukraine varied within 8.55×10^{-6} to $5,19\times10^{-4}$ and was lower by 4 to 5 orders of magnitude as compared with DDT environmental toxicity.

3. Among the studied pesticides, strobilurine fungicides had the least migration probability to groundwater at soil and climatic conditions of Ukraine; among them, pyraclostrobin and picoxystrobin featured the low mobility by K_{oc}, the low leaching probability into groundwater by GUS and low contamination risk for ground- and surface water by LEACH. Azoxysrobin was moderately mobile, with low/moderate leaching capability and low contamination risk for ground- and surface water by K_{oc}, GUS and LEACH, correspondingly. Nicosulfuron and dicamba featured the highest migration within the “soil – water” system; they are very mobile by Koc and have the high contamination risk for ground- and surface water by LEACH. Nicosufluron has also the high leaching probability by GUS.

4. It was found that picoxystrobin and diflufenzopyr were the least hazard pesticides among the studied ones by integral evaluation of the hazard to humans due to the contamination of ground- and surface water (moderately hazardous by integral vector R, hazardous and moderately hazardous by IGCHI) while dicamba, difenoconazole and pymetrozine were the most hazardous (high hazard level by integral vector R, extremely and high-hazardous by IGCHI).

5. Assessment of the hazard to humans caused by the ground- and surface water contamination due to pesticide migration from the soil was not the same by different procedures, they complemented each other

6. While protecting oil crops, it is necessary to limit application of formulations based on dicamba, difenoconazole, pymetrozine and nicosulfuron at the land plots with light soil texture, high groundwater level and close location of surface watercourses. Preference should be given to pesticides with the least contamination hazard for the soil, groundwater and surface water bodies – picoxystrobin, diflufenzopyr, pyraclostrobin.

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