

## Comparative hygienic evaluation of behavior of different pesticides groups in soil, prediction of risk of ground water contamination and its danger for human health in areas with irrigation farming

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**Objective:** A comparative risk evaluation of contamination of the soil and groundwater with fungicides, insecticides and herbicides, and risk assessment of the adverse effects of these substances on human health while contaminated groundwater consumption.

**Methodology:** Field hygienic experiments with studied pesticides were carried out in different soil and climatic zones. Prediction of pesticides migration possibility in groundwater was carried out by Groundwater ubiquity score (GUS) and Leaching potential index (LEACH). For integrated assessment of the potential hazard of pesticide exposure on the human organism when it enters ground and surface waters we used integral groundwater contamination index (IGCHI).

**Results:** Among fungicides, the most resistant were triazoles, herbicides oxyacetamide flufenacet and all studied insecticides. There was

a significant difference between the maximum and minimum  $DT_{50}$  values, in some cases the difference reaches more than 10 times. The evaluation of GUS index showed that risk of leaching into groundwater of fungicides based on paclobutrazol, herbicides based on metribuzin, insecticides based on thiamethoxam during application in soil and climatic conditions of Ukraine is a high (probably leached).

**Conclusion:** The maximum possible concentration of studied groups pesticides in groundwater was significantly lower than allowable, which is associated primarily with low application rates and indicates the relative safety for human health when consuming water, which could be contaminated with test compounds. (Rawal Med J 201;43:129-136).

**Key words:** Groundwater, fungicides, insecticides, herbicides, risk, forecasting, health.

## INTRODUCTION

The term pesticides is a composite term that includes all chemicals that are used to kill or control pests. In agriculture this includes: Herbicides (weeds), Insecticides (insects), Fungicides (fungus), Nematocides (nematodes) and Rodenticides (vertebrate poisons).<sup>1</sup> Pesticides are hazardous to human health and their exposure may lead to acute pesticide poisoning resulting in fatigue, headaches and body aches, skin discomfort, skin rashes, poor concentration, feelings of weakness, circulatory problems, dizziness, nausea,

vomiting, excessive sweating, impaired vision, tremors, panic attacks, cramps, and in severe cases coma and death.<sup>2</sup> Pesticides pose serious threats to both human health and the environment. Ability of pesticides accumulate in the soil may lead to contamination of the environment predominantly ground and surface water.<sup>3-6</sup>

Water pollution is one of the major threats to public health in Pakistan. Drinking water sources, both surface and groundwater are contaminated with coliforms, toxic metals and pesticides throughout the country.<sup>7</sup> But humanity

will not abandon the use of pesticides taking into account, first, constant growing of human population and starvation world problem. According to WHO and UNO, each third person has starvation nowadays and by 2050 the Earth population will increase more than 2 billion, and its food needs will increase by 70 %.<sup>8,9</sup> In experiments in France, 50% reduction in pesticide use lead to wheat production losses by about 2 to 3 millions tons, which represent about 15% of the French wheat export.<sup>3</sup> Aim of this study was comparative risk evaluation of contamination with fungicides, insecticides and herbicides of the soil and groundwater of Ukraine comparing with other countries, as well as risk assessment of the adverse effects of these substances on human health while contaminated groundwater consumption.

## METHODOLOGY

We studied the most widely used chemicals in agriculture classes of *fungicides*: triazoles (epoxiconazole, paclobutrazol, difenoconazole, propiconazole), oxazoles (famoxadone), piperidinyltriazol-isoxazoline (oxathiapiprolin), pyrazolecarboxamide (benzovindiflupyr), amide (cyflufenamid), imidazole (prochloraz); *herbicides*: oxiacetamide (flufenacet), triazinone (metribuzin), bipyridiliums (diquat) and *insecticides*: neonicotinoids (thiamethoxam, imidacloprid).<sup>10-12</sup> Information about the basic physical and chemical properties of the test substances is shown in Table 1.<sup>13</sup>

Field hygienic experiments with studied active ingredients of pesticides were carried out in different soil and climatic conditions of Ukraine, which corresponds to different soil and climatic zones: Polissia (Kiev region or West and North Europe), Forest-steppe (Vinnitsa, Kiev, Poltava region or Central and East Europe) and Steppe (Odessa, Kherson region or South Europe).<sup>13,14</sup> The main characteristics of soil and climatic conditions of these regions have already been

published.<sup>5</sup>

For calculation of a.i. half-life periods ( $DT_{50}$ ) and persistence in soil mathematical modeling method was used. For classification of substances by stability and migration ability in soil two approaches were used: Ukrainian classification of pesticides by the degree of hazard SSaNRN 8.8.1.002-98 and International IUPAC and SSLRC classifications.<sup>15-17</sup>

Prediction of possibility of migration of pesticides in groundwater was carried out by: Groundwater ubiquity score (GUS) and Leaching potential index (LEACH).<sup>18,19</sup> For integrated assessment of the potential hazard of pesticide exposure on the human organism when it enters ground and surface waters, we used integral groundwater contamination index (IGCHI) which includes assessment of 3 indices: LEACH,  $DT_{50}$  in water and allowable daily intake (ADI) on a scale which provides four gradations.<sup>5</sup>

For determination of potential risk to the environment and human health by drinking water containing the pesticide screening model of maximum concentration of a pesticide in groundwater determination SCI-GROW, developed by the Agency for Environmental Protection (EPA) USA, was used.<sup>20</sup> For the evaluation of the parameters of SCI-GROW a method of comprehensive assessment including establishing of the maximum possible daily intake of pesticide with water (MPDIW) and subsequently compared with acceptable daily intake of pesticide with water (ADIW).<sup>21</sup>

## RESULTS

Analysis of physical and chemical properties of the studied pesticides (Table 1) showed that all herbicides, insecticides and most of fungicides had low affinity to lipophilic components according to values of distribution coefficient in octane-water system ( $\log K_{o/w}$ ), except difenoconazole, famoxadone, benzovindiflupyr and cyflufenamid. This index may indicate that the

majority of the compounds will not bind in a soil with lipophilic component. All analyzed fungicides and herbicide flufenacet were insoluble or poorly soluble in water, indicating the possibility of forming by them strong ties with soil components and, consequently, they will be immobile in it. Other studied herbicides and insecticides were soluble and highly soluble in water. Insecticides, fungicide paclobutrazol and herbicides, except diquat, were mobile and moderately mobile in soil (organic carbon adsorption coefficient ( $K_{oc}$ ) below 499), all other fungicides were weakly or not mobile in soil.

Evaluation of the behavior and distribution of studied pesticides in soil only by physical and chemical properties are not sufficient, that is why we have done mathematical modeling of its persistent according to field researches conducted in Ukraine (Table 2). As a result of mathematical modeling of the behavior of the studied compounds in soil the half-life periods ( $DT_{50}$ ) in soil and climatic conditions of Ukraine were calculated (Table 3).

Among fungicides, the most resistant were triazoles class compounds, herbicides oxyacetamide class compound (flufenacet) and all studied insecticides. There was no significant difference between the minimum and maximum  $DT_{50}$  values, obtained in the soil and climatic conditions of Ukraine.

The results of field studies and evaluation of GUS index showed that risk of leaching into groundwater of fungicides based on paclobutrazol, herbicides based on metribuzin, insecticides based on thiamethoxam during application in soil and climatic conditions of Ukraine was high (probably leached). When applying fungicides based on famoxadone, oxathiapiprolin, benzovindiflupyr, prochloraz and insecticides based on diquat risk of leaching from soil to groundwater is low (probably not leached), when applying of fungicides based on epoxiconazole, difenoconazole, cyflufenamid,

herbicides based on flufenacet, insecticides based on imidacloprid risk is negligible risk (negligible probability of leaching). The differences of potential leaching risk can be explained by different stability of abovementioned compounds in different soil types.

Assessment of the possible negative impact on the human body of studied fungicides, insecticides and herbicides during their leaching into the water was made according to SCI-GROW index. It was found that in soil and climatic conditions of Ukraine SCI-GROW index was significantly below 1 mg/l and on the order below similar indicators in other countries. The obtained results can be explained by differences in the maximum application rates, the multiplicity of applications and soil stability of substances.

On the basis the ADI values approved in Ukraine and in the EU, we calculated the allowable daily consumption (ADC) of the studied compounds by human: 60-3600 mg/day and 120-62400 mg/day, respectively (Table 3). Considering that with water in the human body can enter 20% of the pesticide ADC, ADCW values were 12-720 mg/day.

## DISCUSSION

Comparative analysis of the data of field researches, conducted in other countries, has shown that there is a significant difference between the maximum and minimum  $DT_{50}$  values, in some cases the difference reaches more than 10 times.<sup>14</sup> The results of stability of fungicides, insecticides and herbicides, widely used for crops protection in Ukraine, almost coincide with the minimum  $DT_{50}$  values, obtained in soil and climatic conditions of other countries, but the maximum values are significantly different.<sup>14</sup> This difference is caused by the peculiarities of soil types: in most of Ukrainian territory black and sod-podzolic soils, in other countries, where researches have been conducted sandy soils from acidic to mountain.<sup>14,22</sup>

Table 1. Physical and chemical properties of test substances.<sup>13</sup>

Chemical class	Trade name	Chemical name (IUPAC)	lg K <sub>ow</sub>	Solubility in water, mg/l	K <sub>oc</sub> , ml/g
1	2	3	4	5	6
<b>Fungicides</b>					
triazoles	epoxiconazole	(2RS,3SR)-1-[3-(2-chlorophenyl)-2,3-epoxy-2-(4-fluorophenyl)propyl]-1H-1,2,4-triazole	3.3	7.1	1073.0
	paclobutrazol	(2RS,3RS)-1-(4-chlorophenyl)-4,4-dimethyl-2-[(1H-1,2,4-triazol-1-yl)pentan-3-ol	3.11	22.9	400
	difenoconazole	3-chloro-4-[(2RS,4RS;2RS,4SR)-4-methyl-2-[(1H-1,2,4-triazol-1-yl)methyl]-1,3-dioxolan-2-yl]phenyl 4-chlorophenyl ether	4.36	15.0	400-7730
oxazoles	famoxadone	(RS)-3-anilino-5-methyl-5-(4-phenoxypheyl)-1,3-oxazolidine-2,4-dione	4.65	0.059	3847
piperidinyl thiazole isoxazolines	oxathiapiiprolin	1-(4-((5RS)-5-(2,6-difluorophenyl)-4,5-dihydro-1,2-oxazol-3-yl)-1,3-thiazol-2-yl)-1-piperidyl)-2-(5-methyl-3-(trifluoromethyl)-1H-pyrazol-1-yl)ethanone	3.66	0.1749	9673.8
pyrazolcarboxamide	benzovindiflupyr	N-(((1RS,4SR)-9-(dichloromethylene)-1,2,3,4-tetrahydro-1,4-methanonaphthalen-5-yl)-3-(difluoromethyl)-1-methylpyrazole-4-carboxamide	4.32	0.98	3829-5221
amide	cyflufenamid	(Z)-N-[α-(cyclopropylmethoxyimino)-2,3-difluoro-6-(trifluoromethyl)benzyl]-2-phenylacetamide	4.7	0.52	1000-2354
imidazole	prochloraz	N-propyl-N-[2-(2,4,6-trichlorophenoxy)ethyl]imidazole-1-carboxamide	3.5	26.5	2225.0
<b>Herbicides</b>					
oxyacetamide	flufenacet	4'-fluoro-N-isopropyl-2-[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yloxy]acetamide	3.2	56	401
triazinone	metribuzin	4-amino-6-tert-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one	1.65	1165	37.92
bipyridylum	diquat	9,10-dihydro-8a,10a-diazoniaphenanthrene	-4.6	718000	2185000
<b>Insecticides</b>					
neonicotinoid	thiamethoxam	(EZ)-3-(2-chloro-1,3-thiazol-5-ylmethyl)-5-methyl-1,3,5-oxadiazinan-4-ylidene(nitro)amine	-0.13	4100	56.2
	imidacloprid	(E)-1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine	0.57	610	225

Table 2. Conditions of studied pesticides application.

Chemical class	Active ingredient	Preparation	Preparation application rate, l(kg)/ha(tonn) (rate)	Crop	Soil type
1	2	3	4	5	6
<b>Fungicides</b>					
triazole	epoxiconazole	Barclay Korrib	1,5 (2)	wheat	black soil (chernozem)
	paclobutrazol	Setar	0,5 (2)	rape	black soil (chernozem)
	difenoconazole	Dinaly	0,7 (3)	grapevine	black soil on heavy clays
		Cydely Top	0,7 (2)	apple	black soil (chernozem)
		Setar	0,5 (2)	rape	black soil (chernozem)
		Skor	0,5 (3)	tomato	black soil (chernozem)
		Amistar Gold	1,0 (2)	sunflower	black soil (chernozem)
		Magnello	1,0 (2)	wheat	black soil (chernozem)
oxazole	famoxadone	DPX-LVH 88	0,66 (3)	potato	dark chestnut
piperidinyl thiazole isoxazoline	oxathiapiprolin	DPX-LVH 88	0,66 (3)	potato	dark chestnut
pyrazolcarboxamide	benzovindiflupyr	Elatus Ria	0,6 (2)	wheat, barley	black soil (chernozem)
amide	cyflufenamid	Dinaly	0,7 (3)	grapevine	black soil (chernozem) on heavy clays
imidazole	prochloraz	Cidely Top	0,7 (2)	apple	black soil (chernozem)
		Barclay Korrib	1,5 (2)	wheat	black soil (chernozem)
<b>Herbicides</b>					
oxyacetamide	flufenacet	Artist	2,5 (1)	potato	black soil (chernozem)
triazinone	metribuzin	Artist	2,5 (1)	potato	black soil (chernozem)
bipyridylium	diquat	Reglon Forte	1,5 (1)	potato	black soil (chernozem)
<b>Insecticides</b>					
neonicotinoid	thiamethoxam	Cruiser	0,15 (1)	potato	dark-grey+ black soil (chernozem)
		Select Top	2,0 (1)	wheat	black soil (chernozem)
	imidacloprid	Colt Power	0,05 (1)	potato	black soil (chernozem)

Table 3. Application rates, parameters of stability and groundwater migration of studied pesticides.

Active ingredient (a.i.)	Maximal application rate of a.i., kg/ha under maximal application number (MAR)	DT <sub>50</sub> <sup>1</sup> soil, day		DT <sub>50</sub> <sup>2</sup> soil, day		GUS <sup>1</sup>	GUS <sup>2</sup>	SCI-GROW <sup>1</sup> , hg/l	Daily intake with 3 l of water, l/day	SCI-GROW <sup>2</sup> , hg/l	ADI <sup>1</sup> , mg/kg	ADC <sup>3</sup> , hg/ day	ADC with water, hg/day	ADI <sup>2</sup> , mg/kg	ADC <sup>4</sup> , hg/day
		л.г.г.г.	3	4	5	6									
1	2														
<b>Fungicides</b>															
epoxiconazole	0.225		59.1	83.7	44.0	124.0	1.82	2.28	1.59×10 <sup>-02</sup>	0.0477	0.004	240	48	0.008	480
paclobutrazol	0.126		27.2	155.9	3.1	390.0	3.49	3.49	4.57×10 <sup>-02</sup>	0.1371	0.02	1200	240	0.022	1302
difenoconazole	0.370		8.8	70.9	20.0	265.0	1.96	0.90	1.50×10 <sup>-01</sup>	0.4500	0.002	120	24	0.01	600
famoxadone	0.653		13.1	16.9	8.0	104.3	0.48	1.35	2.03×10 <sup>-02</sup>	0.0609	0.01	600	120	0.012	720
1	2		3	4	5	6	7	8	9	10	12	13	14	15	16
oxathiapiprolin	0.059		15.9	18.7	31.5	138.5	0.01	0.43	1.16×10 <sup>-02</sup>	0.0348	- <sup>5</sup>	-	-	1.04	62400
benzovindiflupyr	0.1		6.9	7.2	144.0	501.0	0.26	-	6.55×10 <sup>-04</sup>	0.0019	0.01	600	120	0.05	3000
cyflufenamid	0.066		11.7	22.18	10.2	91.0	1.96	1.85	11.5×10 <sup>-01</sup>	0.3450	0.01	600	120	0.04	2400
prochloraz	0.9		16.33	18.77	1.9	73.2	0.812	1.98	1.41×10 <sup>-02</sup>	0.0423	0.001	60	12	0.01	600
<b>Herbicides</b>															
flufenacet	0.600		27.9	38.8	38.0	43.0	2.1	2.23	1.94×10 <sup>-01</sup>	0.5820	0.004	240	48	0.005	300
metribuzin	0.438		18.6	22.8	5.3	17.7	3.2	2.57	7.58×10 <sup>-01</sup>	2.274	0.004	240	48	0.013	780
diquat	0.600		34.4	98.1	598.0	>1000	-4.2	-6.85	9.00×10 <sup>-03</sup>	0.0270	0.002	120	24	0.002	120
<b>Insecticides</b>															
thiamethoxam	0.090		47.0	48.6	7.0	72.0	3.78	4.69	1.37×10 <sup>-01</sup>	0.4110	0.02	1200	240	0.026	1560
imidacloprid	0.035		33.0	47.1	104.0	228.0	2.6	3.74	9.77×10 <sup>-03</sup>	0.0293	0.06	3600	720	0.06	3600

Notes: <sup>1</sup> - results, obtained in Ukrainian soil and climatic conditions;<sup>2</sup> - literature data <sup>3</sup>;<sup>3</sup> - taking into account ADI value adopted in Ukraine;<sup>4</sup> - taking into account ADI value adopted in EU <sup>13</sup>;

GUS – Ground ubiquity score;

SCI-GROW – Screening concentration in groundwaters;

ADC – acceptable daily consumption (ADI×60);

<sup>5</sup> – pending ADI.



Our data on GUS index evaluation almost coincides with the data obtained in other countries, except difenoconazole, prochloraz, metribuzin and imidacloprid. The differences of potential leaching risk can be explained by different stability of abovementioned compounds in different soil types. The calculation results showed that the values of the maximum possible daily consumption of the pesticide with water (MPDCW) significantly below ADCW according to field researches conducted in Ukraine and other countries. The results indicate a relatively low risk to humans by ingestion of water contaminated with pesticides of studied groups which compares with results for other pesticide groups.<sup>4,21</sup>

## CONCLUSION

Triazole class fungicides (epoxiconazole, paclobutrazol, difenokonazole), oxyacetamide class herbicide (flufenacet) and neonicotinoid class insecticides according its soil stability were classified as stable, pyrazolcarboxamide benzovindiflupyr as unstable and other studied fungicides moderately stable compound. Risk of leaching into groundwater of fungicides based on paclobutrazol, herbicides based on metribuzin, insecticides based on thiamethoxam during application in soil and climatic conditions of Ukraine was high (probably leached). The maximum possible concentration of studied groups pesticides in groundwater was significantly lower than allowable, which is associated primarily with low application rates and indicates the relative safety for human.

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**Conflict of Interest:** None declared

Rec. Date: Jun 16, 2017 Revision Rec. Date: Aug 18, 2017 Accept Date: Oct 4, 2017

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