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Martiianova Yuliia Volodymyrivna
Graduate student of the Department of Hygiene and Ecology № 3,
Bogomolets National Medical University, Ukraine

Korshun Olga Myhailivna
Candidate of Biological Sciences, Senior Research Fellow, Institute of Hygiene and Ecology
Bogomolets National Medical University, Ukraine

Korshun Mariia Myhailivna
Doctor of Medical Science, Professor at the Hygiene and Ecology Department № 3,
Bogomolets National Medical University, Ukraine

RISK ASSESSMENT FOR HUMAN HEALTH BY BICYCLOPYRONE AS A POTENTIAL POLLUTANT OF GROUNDWATER AND SURFACE WATERS IN SOIL AND CLIMATIC CONDITIONS OF UKRAINE

Abstract. *The risk on human health of bicyclopyrone as a potential contamination of groundwater and surface water sources in soil and climatic conditions of Ukraine in comparison with other countries has been assessed. It has been established that bicyclopyrone has a very high level of danger according to the integral danger vector R and is extremely dangerous for humanity (1A class) according to the – integral groundwater contamination hazard index (IGCHI). Comparison of the maximum possible good approximation in the human body of bicyclopyrone in water with an acceptable daily use showed that the potential risk of adverse effects of pesticides on human health (RAEP) bicyclopyrone is acceptable (less than one). The assessment of danger to public health by bicyclopyrone as a contaminant of groundwater and surface water in soil and climatic conditions of Ukraine coincides with the assessment of studies' results in other countries.*
Keywords: *bicyclopyrone, soil, water sources, hazard assessment.*

One of the urgent tasks of public health in the field of pesticides hygiene and toxicology is to minimize the risks arising from the widespread use of chemical plant protection products in modern agriculture. For people who do not have professional contact with pesticides, the main route of entry of the latter into the body is oral. In

addition, 70-80% of the actual daily dose of the vast majority of pesticides enters the human body with a diet, and 20% - with drinking water.

Earlier, based on the results of mathematical modeling, it has been proved that the limiting link of migration from soil to adjacent media is bicyclopyrone – herbicides from the class of tricetone, inhibitor of 4-hydroxyphenylpyruvate dioxygenase plants, there is a system of "soil - groundwater" [1].

Therefore, the aim of this work was to assess the risk on public health of bicyclopyrone as a potential contaminant of groundwater and surface water in soil and climatic conditions of Ukraine in comparison with other countries.

In the first stage, we assessed the risk of groundwater and surface water sources contamination with bicyclopyrone based on the results of studies conducted in different countries with different soil and climatic conditions.

The stability of bicyclopyrone was studied in different types of soils (loam, sand clay loam, clay loam, silt loam, silt clay loam, silt clay, loamy sand) [2]. The half-life (DT50) of the compound varied in a wide range depending on mechanical composition of soil, his pH, organic matter content: in laboratory experiments - 19.8-434 days, in field - 1.7-36 days, which allowed to include bicyclopyrone in stability in soil to both low stable (III class) and highly stable (I class) in laboratory and moderately stable (II class) in kind pesticides according to the International Classification IUPAC [2, 3, 4].

It was found that the sorption coefficient of organic carbon (K_{oc} = 6–500 ml/g [3]) bicyclopyrone is from very mobile (I class) in most soils (17 of 23 tested) to little mobile (IV class) according to the International classification SSLRC (Soil Survey and Land Research Center) [5]. No correlation was found (r = 0.11) between soil organic carbon content and bicyclopyrone adsorption [3].

We calculated the screening index of leaching (LIX) [6], Groundwater ubiquity score (GUS) [7], the leaching index to assess the potential contamination of groundwater and river water ($LEACH_{mod}$) [8] and the maximum possible concentration of bicyclopyrone in groundwater by screening-model (SCI-GROW) [9] in a wide range of soil and climatic conditions.

According to the screening index of leaching (LIX = 0.0000–0.9905),

bicyclopyrone can be classified as an non leaching (in some cases) and as a leaching (in most soil and climatic conditions) pesticide [6]. Leaching potential index GUS of bicyclopyrone (GUS = 0.30-8.50) is estimated from very low (V class) to very high (I class) according to the classification [10].

The risk of potential contamination of river water and groundwater $LEACH_{mod}$ (404.6–714000), which, unlike GUS, takes into account not only DT50 and K_{oc} substance, but also its solubility in water (S_w), is high (I class) according to the classification [8].

The maximum possible concentration of bicyclopyrone in groundwater according to the screening-model (SCI-GROW) depending on soil and climatic conditions varies in a wide range: from 6.41×10^{-4} to 2.52 μg/l. Under the most unfavorable soil and climatic conditions, it exceeds the maximum allowable concentration of pesticide in drinking water (0.0001 mg/dm^3 or 1×10-1 μg / l) by 25.2 times.

Since the above indicators allow predicting the possibility and even the level (including SCI-GROW) of water pollution of groundwater and surface water, but none of them give an assessment of the danger of such pollution for the human body, we used models [11, 12, 13], which link the behavior of the substance in the "soil - water" system with the criteria of toxicity and accumulation, which allows to assess the risk on human health of potential contamination of groundwater and surface water sources due to migration of pesticides from soil.

Methods [11] and [12] use a fundamentally similar approach – a score of 3 criteria: soil mobility, (according to the GUS and $LEACH_{mod}$ indices, respectively), water stability, toxicity and accumulation (by zone of biological effect $Z_{biol.ef}$ and allowable daily intake ADI , respectively) of the substance, while comprehensive assessment method of adverse effects risk of pesticides on human body when washed into water according to [13] is based on comparison of potential exposure (pesticide maximum possible daily intake with water – PMDIW) with pesticide acceptable daily intake with water (PADIW).

It is known that bicyclopyrone is highly stable in water (I class of hazard): the half-life of T50 due to hydrolysis is more than 365 days, in the system "water-

sediment" - 681 days. The substance is low-toxic when administered once in rats' stomachs (on the average lethal dose LD50 > 5000 mg/kg) [2, 3]. The minimum NO(A)EL (No Observed Adverse Effect Level) of bicyclopyrone (0.28 mg/kg) was found in a chronic experiment in male rats [2, 3]. According to the value of the zone of biological effect of bicyclopyrone ($Z_{biol.ef}$ = 17857.1) belongs to the extremely hazardous (I class) substances.

According to the value of the zone of biological effect, bicyclopyrone belongs to extremely dangerous (I class) substances. In Ukraine, the ADI of bicyclopyrone at the level of 0.0003 mg/kg was scientifically substantiated, based on the lowest value of NOAEL in terms of general toxicity and eye effects in a combined study of chronic toxicity and carcinogenicity in male rats (0.28 mg/kg) and a stock ratio 1000.

The potential danger to public health of groundwater pollution by bicyclopyrone according to the integrated danger vector R (144.6–173.2) according to the method [11] was estimated by us as very high regardless of soil and climatic conditions.

In accordance with the method [12] by integral groundwater contamination hazard index (IGCHI), bicyclopyrone (IGCHI = 12 points) was recognized as extremely hazardous for public (1A class).

A comprehensive assessment of danger by bicyclopyrone to human body when it is washed into water according to the method [13] showed that the potential risk of adverse effects of pesticides on public health (RAEP) is less than one (RAEP ranges from 8.3×10^{-5} – 3.2×10^{-1}), is acceptable.

In the second stage, field studies were conducted in soil and climatic conditions of Ukraine, in Kyiv (Skvyra district), Khmelnytsky (Derazhnyansky district) and Cherkasy (Korsun-Shevchenkivsky district) regions. The work with growing corn made before germination or after germination (in the phase of 1-2 leaves, 3-4 or 3-8 leaves of culture) with the preparation Akuron Uno 200 SL, RK (bicyclopyrone, 200 g/l) with a consumption rate of 0.75 l/ha once.

The dynamics of residual amounts of bicyclopyrone in soil was studied. It was found that at harvest time (101–120 days after processing) bicyclopyrone was not detected in soil by high-performance liquid chromatography (detection limit - 0.005

mg/kg).

According to the actual data, the destruction rate constant was calculated (k = 0.0385 ± 0.0038 day-1), the half-lives (DT50 = 18.3 ± 1.9 days), the destruction of 95% of the initial amount of the substance (DT95 = 79.3 ± 8.2 days) and almost complete (99% of the initial amount of the substance) destruction (DT99 = 122.0 ± 12.6 days) destruction of bicyclopyrone in soil. It shows that in soil and climatic conditions of Ukraine bicyclopyrone in terms of soil stability can be attributed to moderately stable (III class hazard) according to current hygienic classification of pesticides in our country [14] and to low-stability (III class) pesticides according to the IUPAC International Classification.

According to the screening index of leaching (LIX = 0.7937–4.3635), bicyclopyrone in soil and climatic conditions of Ukraine can be classified as a leaching pesticide according to [6]. Ability to leach according to the GUS index (1.64–4.07) is rated from low (IV class) to very high (I class) according to classification [10].The risk of potential contamination of surface water and groundwater with bicyclopyrone according to the $LEACH_{mod}$ index (435.54–36295) is high (I class) according to classification [8].

The maximum possible concentration of bicyclopyrone in groundwater according to screening-model (SCI-GROW) varies in a fairly narrow range: from 3.97×10^{-2} to 5.47×10^{-1} μg/l. Under the most unfavorable soil and climatic conditions, it exceeds maximum allowable concentration of pesticide in drinking water (0.0001 mg/dm^3 or 1×10^{-1} μg/l) by 5.5 times.

The results of risk assessment on public health of potential contamination of groundwater and surface water sources due to migration of pesticides from the soil according to the methods [11, 12, 13] are given in the table.

In soil and climatic conditions of Ukraine, the potential danger to public health of groundwater pollution by bicyclopyrone by the integrated danger vector R (R = 144.6–173.2) is estimated as very high; according to the integral groundwater contamination hazard index bicyclopyrone (IGCHI = 12 points) was recognized as extremely hazardous for public (1A class), which coincides with the assessment of studies' results in other countries.

Table

Assessment of the risk on human health of potential contamination of groundwater and surface water sources with bicyclopyrone in soil and climatic conditions of Ukraine

Assessment methodology *	Indicators, units of measurement	Indicator value		Integral assessment	Hazard assessment
		absolute	bali		
R	GUS	1,64–4,07**	30–100**	144,6–173,2**	very high level
	T_{50} in water, day	>365	100		
	$Z_{biol.ef}$	17857,1	100		
IGCHI	$LEACH_{mod}$	435,54–36295**	4	12	1A (extremely hazardous)
	T_{50} in water, day	>365–681**	4		
	ADI, mg/kg	0,0003	4		
RAEP	SCI-GROW, µg/l	$3{,}97\times10^{-2}$–$5{,}47\times10^{-1}$**		$5{,}0\times10^{-3}$–$6{,}8\times10^{-2}$**	acceptable risk
	N, kg/ha	0,15			
	MDIW, µg/day	0,0179–0,2462**			
	ADIW, µg/day	3,6			

Notes:
*1. * – Score for: R – integral danger vector – data from [11], IGCHI – integral groundwater contamination hazard index – data from [12], RAEP – risk of adverse effects of pesticides on human health – data from [13];*
*2. ** – The range of oscillations from minimum to maximum value is given.*

A comprehensive assessment of hazards to human body of bicyclopyrone when washed into water showed that the potential risk of adverse effects on human health (RAEP) is less than one (RAEP ranges from 5.0×10^{-3}– 6.8×10^{-2}), is acceptable.

Therefore, despite the assessment of bicyclopyrone as extremely hazardous to public (1A class) by the integral groundwater contamination hazard index (IGCHI) and very highly hazardous by the integrated danger vector R, comprehensive assessment based on comparison of potential exposure (maximum possible daily intake of pesticide with water) with an acceptable daily intake with water showed that the potential risk of adverse effects on public health (RAEP) of bicyclopyrone is acceptable (less than one). The assessment of danger to public health of bicyclopyrone as a contaminant of groundwater and surface water in soil and climatic conditions of Ukraine coincides with the assessment of the results of studies in other countries.

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