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COMPARATIVE HYGIENIC RISK ASSESSMENT OF GROUNDWATER CONTAMINATION BY HERBICIDES OF DIFFERENT CHEMICAL CLASSES AND HAZARD PREDICTION FOR HUMAN AFTER CONSUMPTION OF CONTAMINATED WATER

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Abstract

In the structure of main groundwater pollutants leading position is occupied by chemical pesticides. Herbicides are among the most widely used classes of pesticides, according to application technology introduced directly into the soil. Migrating on the soil profile, they create a danger of groundwater contamination that requires their constant control and monitoring. Objective – comparative evaluation of risk of adverse effects on human health by drinking of water contaminated with the most common herbicides. We have studied representatives of herbicides extensively used in agriculture: chloroacetamides; sulfonil-carbonyl-triazolinone, oxazoles, triketones, sulfonylurea, phosphonoglycine. Prediction of migration opportunities in groundwater of studied herbicides was carried out by GUS – Groundwater Ubiquity Score. For determination of potential risk to human health by drinking of water containing pesticides screening model of maximum concentration of pesticide in groundwater determination (SCI-GROW) was used. For the evaluation of the parameters of

SCI-GROW a method of comprehensive assessment developed by us has been used. It is based on establishing of maximum possible daily intake of pesticide with water and subsequently comparing with acceptable daily intake of pesticide with water. It was established that in soil and climatic conditions of Ukraine for most of the test substances probability of leaching into groundwater is negligible; in conditions of other European countries – risk of leaching is low. Maximum possible concentration of the test herbicides in groundwater are insignificant and are much lower of acceptable, which is associated primarily with low application rates and indicates relative safety for human health intakes such water.

Key words: groundwater, herbicides, risk, maximal concentration, allowable intake.

ПОРІВНЯЛЬНА ГІГІЄНІЧНА ОЦІНКА РИЗИКУ ЗАБРУДНЕННЯ ПІДЗЕМНИХ ВОД ГЕРБІЦИДАМИ РІЗНИХ КЛАСІВ ТА ПРОГНОЗ НЕБЕЗПЕКИ ДЛЯ ЛЮДИНИ ПРИ СПОЖИВАННІ ЗАБРУДНЕНОЇ ВОДИ

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У статті представлені порівняльні результати гігієнічної оцінки ризику забруднення підземних вод гербіцидами різних хімічних класів і прогнозування небезпеки для людини при вживанні забрудненої води; надані рекомендації щодо застосування таких гербіцидів

Ключові слова: ґрунтові води, гербіциди, ризик, максимальна концентрація, допустиме надходження.

Nowadays almost 70 % of population of Ukrainian villages and towns and about 65 % - of other European countries population consume drinking water from shaft wells (ground water) or artesian wells (deep water horizons). The probability of groundwater contamination is high enough because groundwaters have different origins: the vast majority of them formed by atmospheric precipitations by filtration through soil layer (infiltration water) or due to condensation of water vapors directly into the ground (condensing water) [1, 91-96].

In the structure of the main groundwater pollutants leading position occupied by chemical pesticides, which can have adverse effects on human health [2, 3]. Particularly, herbicides, which are among the most widely used classes of pesticides in Ukraine (more than 700 preparations are registered and used) and the world [2, 3], according to application technology introduced directly into the soil. Migrating on the profile of the soil, they create a danger of groundwater contamination that requires their constant control and monitoring [4, 67-69; 5, 339-353].

Objective – comparative evaluation of the risk of adverse effects on human health by drinking water contaminated with the most common herbicides used in agriculture.

Materials and methods. We have been studied extensively used in agriculture representatives of the most promising chemical classes of herbicides: chloroacetamides (acetochlore, dimetachlor, propizochlor, S-metolachlor, metasachlor); sulfonil-carbonyl-triazolinone (thiencarbazone-methyl) oxazoles (topramezone, isoxaflutole) triketones (mesotrione), sulfonylurea (foramsulfurone, iodsulfurone methyl-sodium), phosphonoglycine (glyphosate).

Information on basic physical and chemical properties of the studied herbicides shown in Table 1 [3].

During the last 10 years at the Hygiene and Ecology Institute of the O.O. Bohomolets National Medical University stability parameters aforementioned herbicides in soil and climatic conditions of Polissya (Kyiv region), Forest-steppe (Vinnitsa, Kiev, Poltava region) and Step (Odessa, Kherson region) have been studied.

Prediction of migration opportunities in groundwater of studied herbicides in the soil and climatic conditions of Ukraine was carried out by a number of indicators.

Leaching potential index (GUS – Groundwater Ubiquity Score) [5, 341-349] was calculated by the formula:

$$GUS = \log DT_{50} \times \left[4 - \log K_{oc}\right]$$

where DT_{50} – stability (the period of semi destruction) in soil, day;

K_{oc} – organic carbon sorption coefficient.

If the value of GUS> 2,8 – pesticide is probably leached into groundwater; if <1,8 – pesticide is probably not washed into groundwater; 1,8–2,8 – possibility of leaching of pesticides in ground water is negligible.

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 [6, 41-43]. This index takes into account the rate of degradation of the substance in soil organic carbon sorption coefficient, application rate and frequency of pesticide use. In result of the calculation we get the highest possible concentration of substances in the groundwater in mg/l.

For the evaluation of the parameters of SCI-GROW a method of comprehensive assessment of possible adverse effects of pesticides on humans during their leaching into the water developed by us has been used. It is based on establishing of the maximum possible daily intake of pesticide with water (MPDIW) and subsequently compared with acceptable daily intake of pesticide with water (ADIW). It consists of two stages.

In the first, using a computer program provided on the official website of EPA, the actual SCI-GROW index was calculated. The maximum possible daily intake of pesticide with water (MPDIW) was established by the equation:

$$MPDIW = SCI\text{-}GROW \times V \ (\mu g/day), \text{ where}$$

SCI-GROW – screening concentrations of pesticides in groundwater, μg/l;

V – daily intake of water by human, l (3 l – in temperate climate, 5-10 liters – in hot climate).

In the next stage permissible daily intake of pesticide (PDI) was established by equation:

$$PDI = ADI \times M \times 1000 \ (\mu g/day), \text{ where}$$

ADI – acceptable daily intake of pesticide, mg/kg;

M – average weight of person (60 kg);

1000 – factor for conversion in micrograms.

The acceptable daily intake of pesticide with water (ADIW) was calculated by the equation:

$$ADIW = PDI \times 0{,}2.$$

Then the values of MPDIW and ADIW were compared.

Risk considered acceptable if obtained value (P) ≤ 1.

Results and discussion. Results of mathematical modeling of data of field studies in soil and climatic conditions of Ukraine, allowed to calculate the half life periods of studied compounds in soil (DT_{50}) (table 2). Statistical analysis of the results showed that DT_{50} in soil of substances of most commonly represented class of chloroacetamides practically did not differ ($p<0{,}05$). This made it possible to calculate the average DT_{50} for substances of specified class – 21,38 ± 8,02 days.

The obtained results indicate that features of the chemical structure and physico-chemical properties of these substances from chloroacetamides chemical class not affect their rate of metabolism in the soil. Also, the findings show that the most stable in objects of agrocenosis were chloroacetamides – propizochlor, S-metolachlor, metasachlor and sulfonil-carbonyl-triazolinone thiencarbazone-methyl.

Considering that during application of pesticides, especially of soil herbicides, the main source of groundwater contamination is actually soil we conducted a risk assessment of a possible contamination of groundwater use GUS index in soil and climatic conditions of Ukraine and other European countries (table 2).

It was established that the application of pesticide products based on metasachlor leaching to groundwater is possible, while glyphosate is probably not leaching into groundwater in a soil and climatic conditions of Ukraine. The probability of leaching into groundwater of other representatives of chloroacetamides (acetochlore, dimetachlor, propizochlor, S-metolachlor) and herbicides of other studied classes – is negligible.

The risk of leaching from the soil of preparations based on topramezone in other European countries is high (probably leached), S-metolachlor, metasachlor, thiencarbazone-methyl – is average (probability of leaching is negligible), for other of substances – is low (probably not leaching) [3]. A higher GUS value of topramezone is probably due to its greater stability in soil and climatic conditions of Northern and Western Europe [3]. The difference of the potential risk of leaching in soil of Ukraine and other European countries of other studied substances, including minor differences in their stability in soil, can be explained by peculiarities of application. Namely: preparations application rates, terms and multiplicity of applications.

Table 1

Physical and chemical properties of the test substances [3]

Trade name	Chemical name (IUPAC)	lg P Kow	Solubility in water, mg/l	K_{oc}
chloroacetamides				
acetochlore	2-chloro-*N*-ethoxymethyl-6'-ethylacet-o-toluidide	4,14	282	156
dimetachlor	2-chloro-*N*-(2-methoxyethyl)acet-2',6'-xylidide	2,17	2300	69
propizochlor	2-chloro-6'-ethyl-*N*-isopropoxymethylacet-ortho-toluidide	3,3	90,8	291
S-metolachlor	mix of: (a*RS*,1*S*)-2-chloro-6'-ethyl-*N*-(2-methoxy-1-methylethyl)acet-o-toluidide and (a*RS*,1*R*)-2-chloro-6'-ethyl-*N*-(2-methoxy-1-methylethyl)acet-o-toluidide	3,05	480	226,1
metasachlor	2-chloro-*N*-(pyrazol-1-ylmethyl)acet-2',6'-xylidide	2,49	450	54
sulfonil-carbonyl-triazolinone				
thiencarbazon-methyl	methyl 4-[(4,5-dihydro-3-methoxy-4-methyl-5-oxo-1*H*-1,2,4-triazol-1-yl)carbonylsulfamoyl]-5-methylthiophene-3-carboxylate	-1,98	436	100
oxazoles				
topramezone	[3-(4,5-dihydro-1,2-oxazol-3-yl)-4-mesyl-o-tolyl](5-hydroxy-1-methylpyrazol-4-yl)methanone	-1,52	100000	15,0-296,7
isoxaflutole	(5-cyclopropyl-1,2-oxazol-4-yl)(α,α,α-trifluoro-2-mesyl-p-tolyl)methanone	2,32	6,2	112
triketones				
mesotrione	2-(4-mesyl-2-nitrobenzoyl)cyclohexane-1,3-dione	0,11	160	80
sulfonylurea				
foramsulfurone	1-(4,6-dimethoxypyrimidin-2-yl)-3-[2-(dimethylcarbamoyl)-5-formamidophenylsulfonyl]urea	-0,78	3293	78
iodsulfurone methyl-sodium	sodium ({[5-iodo-2-(methoxycarbonyl)phenyl]sulfonyl}carbamoyl)(4-methoxy-6-methyl-1,3,5-triazin-2-yl)azanide	1,59	25000	45
phosphonoglycine				
glyphosate	*N*-(phosphonomethyl)glycine	-3,2	10500	21699

Table 2

Conditions of application, stability and migration parameters in the groundwater of the studied pesticides

Active ingredient	Maximum application rate of active ingredient, kg/ha under maximal multiplicity of applications	τ_{50}^{1} soil, day	τ_{50}^{2} soil, day	GUS^{1}	GUS^{2}	SCI-GROW[1], µg/l	Daily intake with 3 l of water, µg/day	SCI-GROW[2], µg/l	PDI[3], µg/day	PDI with water, µg/day	PDI[4], µg/day
acetochlore	2,700	15,1	12,1	2,1	1,58	$1,43\times10^{-1}$	0,429	$2,58\times10^{-2}$	60	12	220
dimetachlor	1,200	15,2	3,2	2,6	1,76	$1,14\times10^{-1}$	0,342	$8,68\times10^{-3}$	600	120	6000
propizochlor	2,160	34,6	15,0	2,4	1,36	$2,65\times10^{-1}$	0,795	$1,26\times10^{-2}$	600	120	1500
S-metolachlor	1,920	19,5	21,0	2,1	1,91	$8,00\times10^{-2}$	0,240	$4,85\times10^{-2}$	600	120	6000
metasachlor	1,250	22,5	6,8	3,1	2,17	$2,70\times10^{-1}$	0,810	$4,73\times10^{-2}$	1800	360	4800
thiencarbazone-methyl	0,045	19,3	17,0	2,6	2,46	$0,00\times10^{+0}$	0,000	$1,03\times10^{-1}$	3000	600	13800
topramezone	0,075	15,7	45,2	2,40	5,06	$0,00\times10^{+0}$	0,000	$0,567\times10^{-1}$	30	6	60
isoxaflutole	0,1125	7,9	1,3	1,80	0,59	$0,00\times10^{+0}$	0,000	$1,28\times10^{-3}$	1200	240	1200
mesotrione	0,110	12,2	5,0	1,97	1,47	$0,00\times10^{+0}$	0,000	$4,13\times10^{-3}$	60	12	600
foramsulfurone	0,045	14,7	5,5	2,8	1,56	$0,00\times10^{+0}$	0,000	$4,63\times10^{-3}$	30000	6000	30000
iodsulfurone methyl-sodium	0,0015	5,0	8,0	2,8	0,71	$0,00\times10^{+0}$	0,000	$1,64\times10^{-3}$	18000	3600	1800
glyphosate	1,6654	5,2	12,0	0,9	-0,36	$6,00\times10^{-3}$	0,018	$5,35\times10^{-3}$	600	120	18000

Notes:
[1]- results, obtained in soil and climatic condition of Ukraine;
[2] – literature data [3];
[3] – according to the ADI value approved in Ukraine;
[4] – according to the ADI value approved in EU [3];
GUS –index of potential leaching;
SCI-GROW – screening of concentration in groundwater;
ДДН – permissible daily intake.

It should be noted that in general the risk of groundwater contamination for herbicides is higher than for fungicides, both in the soil and climatic conditions of Ukraine and other European countries [7, 102-105].

To assess a possible negative impact of pesticides on humans during their leaching into the water, we calculated SCI-GROW index. It was determined that in the soil and climatic conditions of Ukraine the maximum possible concentration of chloroacetamide herbicide are on (1–2) orders higher than in other countries; glyphosate – on one level; the rest of the test substances – much lower and almost equal to 0 (diag. 1). Such differences of various herbicide concentrations in Ukraine groundwater and their differences from concentrations in other European countries are explained by, primarily, significant differences in maximum application rates, given the multiplicity of applications and, in some cases, different stability of substances in the soil. Also should be mentioned that in none of cases concentrations the test substances in groundwater did not exceed 1 μg/l.

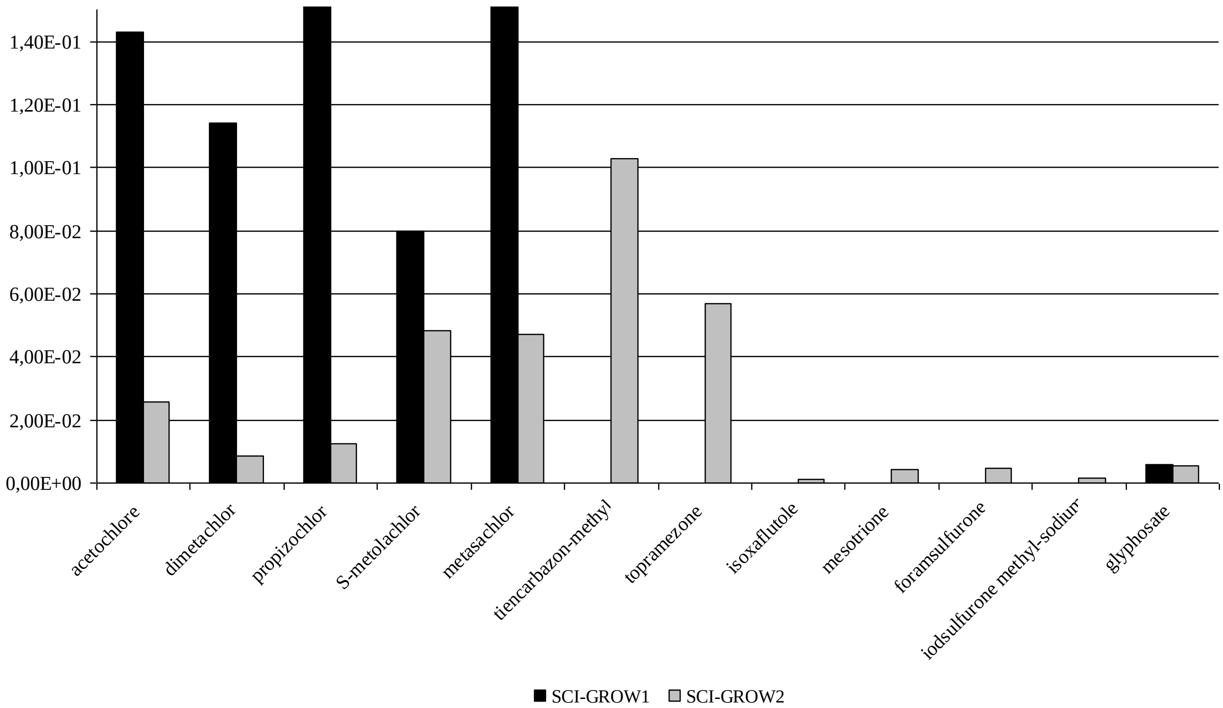

Diagramme 1. The maximum possible concentration of the test substances in groundwater

The resulting maximum concentrations of substances were converted on the average daily water consumption – 3 l (table 2). With this conversion the maximum concentrations values of chloroacetamides and glyphosate in water were slightly increased, but none of them was greater than 1 μg/l; concentrations to the rest of the studied herbicides were equal 0.

In the next stage we calculated the permissible daily intake of the test substances in the human body. The received values range from 60 to 30000 μg/day.

Based on the principles of integrated hygienic regulation adopted in Ukraine, intake with water in the human body can enter 20 % of the PDI of pesticide. Thus, calculated ADIW (table 2) ranges from 6 to 6000 μg/day. The calculation results and the comparison of values showed that the MPDIW values are much lower than ADIW.

It should be noted that studied herbicides by integral hazard index after falling into the water is dangerous, due to their stability in water, high toxicity and high probability of leaching into groundwater and surface water [8, 155-156].

However, the obtained results show that the maximum possible concentration of the studied herbicides in groundwater are much lower than permissible, which is associated primarily with low application rates and indicates the relative safety to humans by drinking water, which could get test compound while their application in agriculture against weeds.

Conclusion. 1. It was established that in soil and climatic conditions of Ukraine for most of the test substances, except metasachlor and glyphosate, probability of leaching into groundwater is negligible; in conditions of other European countries – for most of test substances risk of leaching is low, except topramezone (probably leached) and S-metolachlor, metasachlor, thiencarbazone-methyl (probability of leaching is negligible).

2. It was established that the maximum possible concentration of the test herbicides in groundwater are insignificant and are much lower of acceptable, which is associated primarily with low application rates and indicates relative safety for human health in the use of water, which could get test compound.

3. Taking into account high danger to human health by drinking of water containing studied herbicides, and their low concentration in current application rates is necessary to limit application rates and increasing of multiplicity of applications of such preparations in areas with a high standing of groundwater and close location of surface water bodies.

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