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ECOLOGICAL SAFETY OF PESTICIDE USE IN UKRAINE

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Abstract. The purpose of the study is to determine the levels of hazardous pesticides used in Ukraine and the world and to identify the most dangerous of them.

The main agrochemical manufacturers of Ukraine are analyzed and a list of active pesticide substances is made. The ecotoxic method has been used and the list of the most environmentally hazardous pesticides for the environment and humans has been established. The mechanism of increasing environmental safety by using different pesticides on agricultural lands with acid and alkaline soils is proposed.

Key words: pesticides, ecotoxic, ecological safety, half-life.

Introduction

Thousands of pesticide brands from many manufacturers are used in the world. New, more effective pesticide mixtures are constantly being developed and registered in Ukraine. However, there are relatively few active pesticide substances.

It is well-known that there is a danger to the environment and human health from the use of pesticides, but unexplored dependencies of residual activity of pesticides on objects of the environment.

Actuality: when using pesticides the main parameter of danger is LD50 on rats or other warm-blooded ones. However, when determining toxicity, such indicators as exposure time or volume of pesticides are not taken into account. Quite often, very toxic pesticides are rapidly decomposed in the soil and vice versa, low toxicity pesticides poison the environment for months or even years.

Purpose: the purpose of this work is to determine the levels of hazard of pesticides used in Ukraine and in the world and to identify the most dangerous of them.

The main objectives of the study include: to analyze the existing trade marks of pesticides and their active substances; analyze the structure and properties of active substances; calculate the environmental toxicity of pesticides and identify the most dangerous of them.

In the course of research, systematic, statistical and analytical methods for collecting and interpreting toxicity data of pesticides have been used

Experimental part

Although there is a great number of patented brands of pesticides, their chemical composition is not significantly different. The pesticide formulations that are identical in composition are patented under different names for generating profits without paying the patent owner interest and, accordingly, for obtaining additional profits. Typically, the active substance in pesticides from different manufacturers may be similar. The difference is the ratio of the active substance to the solvent, the amount and composition of the solvents, the mixture in a certain ratio of several active substances of pesticides.

Table 1 lists the trade names of pesticides used in Ukraine and supplied by international giants of chemical production.

Table 1

List of pesticides of the largest chemical producers imported into Ukraine [1]

DUPONT	Akanto Plus, Koragen, Thanas, Task Extra, Granstar Gold, Titus Extra, Harmony, Salsa, Express, Vareon;
BAYER	Herbicides: Adeno, Aptej, Arcan, Artist, Achiba, Basta, Betanal Expert, Betanal Max Pro, Galaxy Ultra, Grodil Maxi, Zenkor Likvid, Kapuero, Laudis, Master, Master Power, Maxi Moks, Merlin, Puma Super, Tortil, Tselmitron , Chelende; Insecticides: K-Apollo EC25, K-Obiol ULV6, Belt, Biscay, Decis F-Suite, Decis Prophy, Envidor, Calypso, Connecto, Confidor, Movento, Proteus; Fungicides: Aviator Xpro, Alliet, Anthracite, Blue Bordeaux, Deorozal, Infinito, Consento, Coronet, Luna Expirienes, Luna Senseihn, Madison, Melody Duo, Ziram, Nativo, Nautil, Pasadoble, Previkuur Energy, Porpulse, Skyway Xpro, Scala, Soligor , Sphere Max, Teddor, Tilmor, Falcon, Fandango, Flint Star, Folikur;
MONSANTO	Roundup, Hernes, Monitor, Guardian Tetra;
CHEMINOVA	Fungicides: Impact K, Impact T, Impact 25, Impact 500; Insecticides: Vanteks, Varand 200, Danadim, Zolon, Fufanon;

Continuation of table 1

	Herbicides: Ador 750, Glyphos Super, Lenacyl Beta, Nikit 240, Wipers, Forcium Vinitsit, Vinyl 050
BASF	Fungicides: Abakus, Alterno, Kapalo, Karambra Turbo, Pictor, Sigun, Sistiv, Cabrio Top, Osiris Star; Herbicides: Butizan Avant, Euro-Leting, Nopasaran, Pulsar 40, Regalis.
Syngenta	This company in Ukraine has about 600 different mixtures of pesticide preparations under different names.

After analyzing the chemical composition of these pesticides and their active substances (AS), it has been found that in most of them about 30 ASs are used (Table 2, 3, 4). Basically it is phosphorus-containing insecticides and herbicides containing chlorine and heavy metals.

Assessment of the potential risk of using pesticides and secondary compounds for ecosystems and biocenoses was conducted using the method [2, 3], which provides for the determination of the eco-toxicological hazard of eco-toxicity (E), taking into account the norms of expenditure (N), persistence (P) and LD_{50} at oral intake of substances into the body of white rats. For eco-toxicity unit eco-toxicological danger of DDT (Dichlorodiphenyltrichloroethane) was accepted at the rate of consumption of 1 kg / ha, persistence – 312 weeks and LD_{50} – 300 mg / kg. Eco-toxicity allows comparing the eco-toxicity of the tested substance with the eco-toxicity of DDT and, accordingly, assessing the relative risk of environmental contamination with this substance.

Calculation was carried out according to the formula:

$$E = \frac{P \times N}{LD_{50}}, \qquad (1)$$

where P – period of half-disappearing substances from the environment, weeks; N – average rate of drug consumption, kg/ha; LD_{50} is the average lethal dose at oral intake by rats, mg / kg.

When a pesticide mixture is applied to agricultural crops, the active ingredient of the pesticide is immediately exposed and gradually split into metabolic products. However, the decay rate of a pesticide is fundamentally different, depending on the conditions of splitting. As a rule, most pesticides are last entered approximately 14–21 days before harvesting. During this period pesticides are split (in vivo) and are removed from agricultural crops to relatively safe levels for human health. However, outside the living cell, the speed of the half-decomposition of the active substance of the pesticide can be tens of times slower and amount many months or even years. Also, this rate depends on the physical and chemical parameters of the environment, the main of which for pesticides is pH. Some pesticides split better in alkaline soils, while others in acidic ones. Table 2 shows the intervals of pesticides' half-life-persistence.

We will analyze ecotoxicity of each of them separately according to the effect of pesticides on environmental objects. Table 1 shows the estimated ecotoxicity of insecticides:

Table 2

Toxicological properties of insecticides

International name of the compound (Ukrainian common name)	LD_{50}, mg / kg	Average consumption rate (N), kg / ha	Persistence (R), weeks	Class of danger	Risk phrases**	Environmental hazards (E), ecotox
Acephate (Acetamidophos)	1400	1.31	0.42–0.84	III	Xn, N: R 22	$3.93\ 10^{-4}$–$7.86\ 10^{-4}$
Bifentrin (Talstar)	55	0.4	4.3–8.7	I	Xn: R22, R65	$3.1273\ 10^{-2}$–$6.3273\ 10^{-2}$
Carbaryl (Karbatots)	850	8	1–4	II	Xn, N, Carc Cat. 3.: R22, R36/37, R40, R50	$9.412\ 10^{-3}$–$37.647\ 10^{-3}$
Fipronil	750	0.2	4.8–17.4	II	Xn: R10, R20/21/22, R36,	$1.28\ 10^{-3}$–$4.64\ 10^{-3}$
Imidacloprid (Confidor)	131	1	14.2–27	II	T: R23/25-48	0.108397–0.206107
Malathion (Carbofos)	400	0.8	0.14–0.43	II	F,Xn,N: R11, R38, R50/53, R65, R67	$2.8\ 10^{-4}$–$8.6\ 10^{-4}$
Permetrin	1725	0.1	2–4	III	Xn: R20/22 R43 N;R50/53	0.000116–0.000232
Trichlorfon (Chlorophos)	660	8.8	0.42–3.85	II	Xn, N: R21/22, R26, R36/38, R43, R50	$5.6\ 10^{-3}$–$51.333\ 10^{-4}$

Note: Xn – Harmfulness, T – Toxicity, Xi – Irritation, N – Environmental hazards, Carc. Cat is carcinogenicity, Muta. Cat – mutagenicity.

* The consumption rate (N) for pesticides is averaged.

** Risk Statements – Standard risk factors for handling hazardous substances set out in Annex III of Directive 67/548 / EEC of the European Union and reissued in Directive 2001/59 / EC [4, 5]. Generally, risk phrases are written on the packaging of pesticides and all other hazardous and harmful substances.

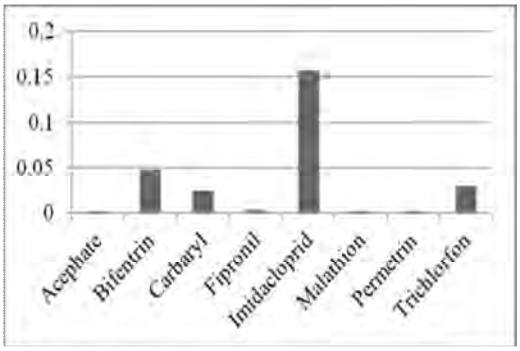

Fig. 1. Diagram of relative ecological toxicity of insecticides

Fig. 1 shows that insecticide, which has the greatest environmental pressure, is imidacloprid, which is produced under the brand name Confidor (Bayer). It is used to combat Colorado bugs, aphids, bastard insects, and others. This pesticide is widely used in Ukraine for the protection of insects from potato and tomato harvest, which also indicates its prevalence. In terms of toxicity, imidacloprid is classified as the 2nd class of danger product and is less toxic than, for example, Bifentrine, which belongs to the 1st class of danger.

Table 3

Toxicological properties of herbicides

International name of the compound (Ukrainian common name)	LD_{50}, mg / kg	Average consumption rate (*N*), kg / ha	Persistence (*R*), weeks	Class of danger	Risk phrases**	Environmental hazards (*E*), ecotox
Benfuralin	3000	1	8.57–18.8	III	T, N: R21, R23/25, R50/53.	$28.57\ 10^{-4}$ – $62.67\ 10^{-4}$
Bensulide	270	5.5	12.85–17.10	II	R22	0.2617–0.3483
Clopyralid	4300	0.56	5–5.7	III	Xi,N: R41-51/53	$6.51\ 10^{-4}$– $7.42\ 10^{-4}$
Dicamba	1300	2	2–2.2	III	Xn,N,F: R22-41-52/53-36-20/21/22-11	$30.77\ 10^{-4}$ – $33.85\ 10^{-4}$
Diquat Dibromide	120	2	10.57–38.57	II	T+, T, Xn, Xi, N: R26, R48/25, R22, R43, R36/37/3, R50, R53	0.1761–0.6428
Dithiopyr	5000	0.3	3.57–9.85	III	R36/38, R43, R50, R53	$2.14\ 10^{-4}$ – $5.91\ 10^{-4}$
Fluazipop-p-butyl	3528	2	2–3	III	R63, R65, R66, R50/53	$11.34\ 10^{-4}$ – $17.01\ 10^{-4}$
Gliphosate	3800	1	2.85–14.2	III	Xi, N: R41, R51/53	$7.5\ 10^{-4}$– $37\cdot10^{-4}$
Imazapyr	5000	2.8	3.57–20.1	III	R36/38, R52/53	$19.99\ 10^{-4}$– $112.5\ 10^{-4}$
Isoxaben	5000	1.12	12.85–17.1	III	N: R50/53	$28.78\ 10^{-4}$– $38.3\ 10^{-4}$
MCPA	765	1.5	3.57–4.28	II	R22 R38 R41 R50/53	$70\ 10^{-4}$– $83.92\ 10^{-4}$
Mecroprop (MCPP)	930	2.05	3–3.42	II	Xn,N,F: R22-38-41-50/53-52/53-36-20/21/22-11	$66.13\ 10^{-4}$– $75.39\ 10^{-4}$
Pendimethalin	5000	1.1	10.7–12.8	III	R22, R43, R65, R66, R51/53	$23.54\ 10^{-4}$– $28.16\ 10^{-4}$
Triclopyr	729	4	0.4–0.6	II	R22	$21.95\ 10^{-4}$– $32.92\ 10^{-4}$
Trifluralin	500	1.5	8–9	II	Xi;N,Xn: R36-43-50/53-20/21/22-11-40	0.024–0.027
2,4-D	375	0.5	1.42–1.57	II	R22 R37 R41 R43R52/53	$18.93\ 10^{-4}$– $20.93\ 10^{-4}$

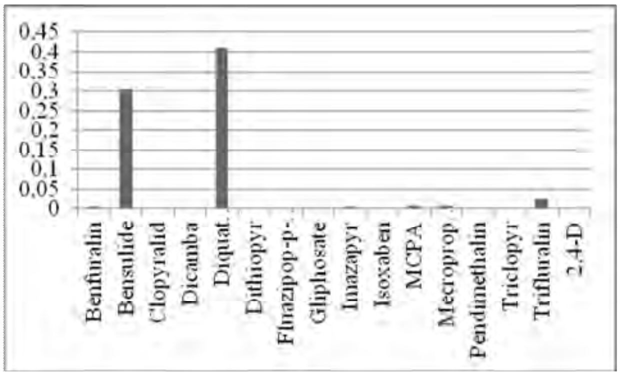

Fig. 2. Ecological toxicity of herbicides

Among the herbicides on the order of importance are 2 pesticides – Bensulide and Dikvat Dibromid. Bensulide is a part of many pesticidal mixtures of various manufacturers by the names: Commercial names – Betamek, Betasan, Disan, Exportsan, Prefar, Presan. It is used for struggle with annual grasses, broadleaf weeds. The main manufacturer is Basf and PBI Gordon.

Dicmat Dibromide is used mainly as desiccant of various storm (Syngenta). In Ukraine there are 23 titles, including Santum, Boomerang, Dikvat M, Diglon, Russell, Priam, Rhistjant and others.

Table 4

Toxicological properties of fungicides and other pesticides

International name of the compound (Ukrainian common name)	LD_{50}, mg / kg	Average consumption rate (*N*), kg / ha	Persistence (*R*), weeks	Class of danger	Risk phrases **	Environmental hazards (*E*), ecotox
Azoxystrobin	5000	0.15	1.6–1.8	III	N,T: R23-50/53	$0.48\ 10^{-4}$– $0.54\ 10^{-4}$
Myclobutanil	1360	0.2	9.42–10	III	Xi, Xn, N: R22, R36,, R50/53, R63.	$13.85\ 10^{-4}$– $14.71\ 10^{-4}$
Propiconazole	1517	2	6.12–10	III	Xn,N,T: R22-43-50/53-39/23/24/25-23/24/25-11	$80.69\ 10^{-4}$– $131.8\ 10^{-4}$
Thiophanate methyl	6640	0.5	1	III	N,Xn: R20-43-50/53-68	$7.53\ 10^{-5}$
Ziram	1400	2	7–7.4	III	T+: R26; R22; R48/22; R37; R41; R43	0.01–0.0105

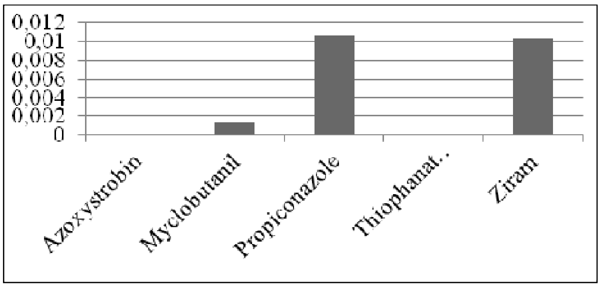

Fig. 3. Ecological toxicity of fungicides

Proprionazole and Ziram are fungicides for the control of various fungi (Bayer). These pesticides refer to the 3rd class of danger and they are safer compared to insecticides and herbicides.

Results and discussion

Therefore, in order to i raise the level of environmental safety, it is necessary to take into account the data of the formulas of ecological toxicity and, if possible:

– to use analogs with lower toxicity values instead of ecotoxic pesticides;

– to reduce the half-life of the most toxic pesticides by introducing them into crops growing on acid or alkaline soils. Under such conditions, the half-life and ecotoxicity of pesticides can be reduced tens of timeds with the constant effectiveness of the pesticide;

– to control the value of pesticide expenditure per unit area;

– to use mixtures of pesticides that are much more effective, and therefore, are introduced in much smaller quantities, which reduces ecotoxicity.

With slight deviations in the acidity of soils, the half-life is significantly reduced by increasing the chemical reactions of hydrolysis in the soil. For example, for the insecticide imidacloprid (Confidor), the half-life decreases from 27 weeks to 4.2 weeks at pH values less than 5 or more than 9 [6]. Some pesticides are resistant to acidic soils and the others, on the contrary, to alkaline environmental conditions. So picking a pesticide according to the soil parameters can significantly increase environmental safety and reduce ecotoxicology.

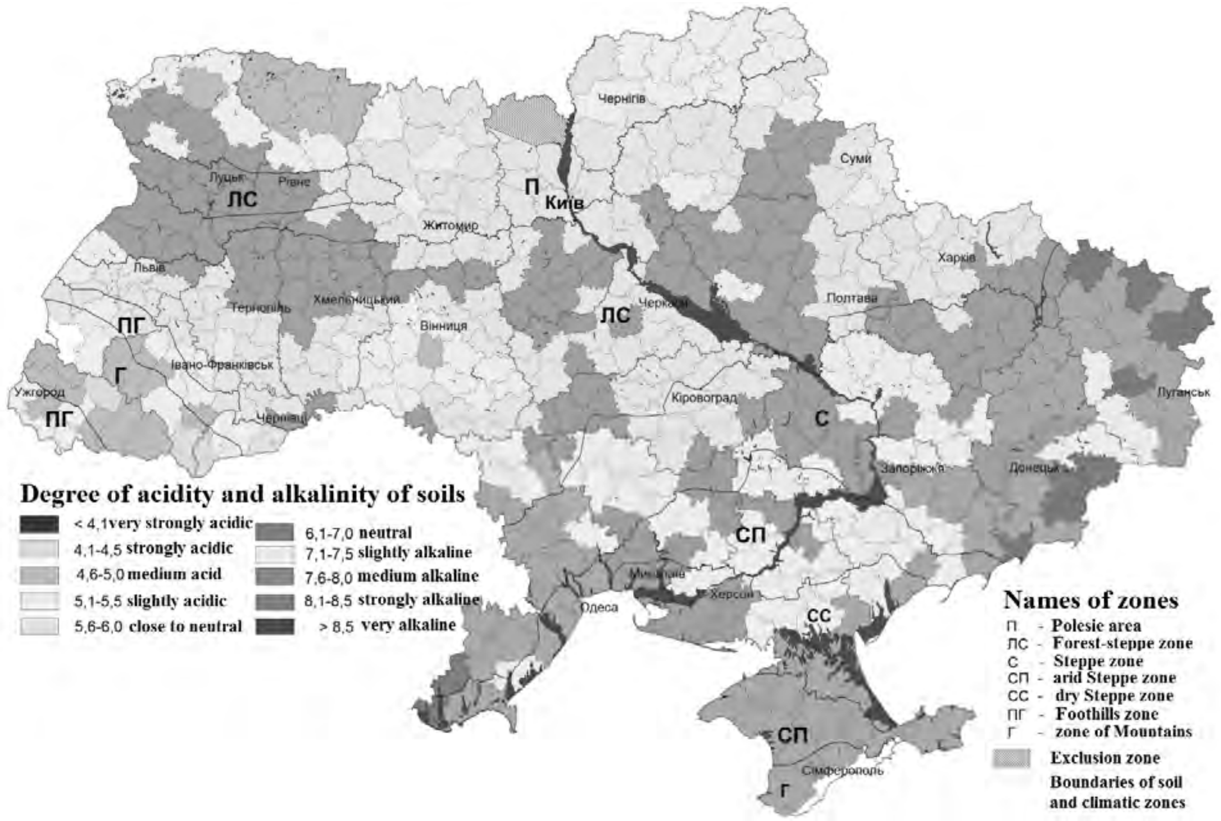

Fig. 4. The value of soil acidity in Ukraine according to agrochemical passport data 2006–2010

Conclusions

The data obtained radically change the attitude towards pesticides that are considered dangerous for the environment and human beings. Thus, among the 30 herbicides most widely used in Ukraine and the world Bensulide and Dikvat dibromid, as well as insecticides Imitacloprid and Bifenthrin are poisonous for the environment and humans.

For the first time, a methodology for calculating the eco-toxicity of pesticides has been used to identify the most dangerous for the environment and humans, which will take into account the existing danger and reduce their use.

For the first time, the method of calculating the ecotoxicity of pesticides has been used to adjust the conditions for the introduction of pesticides into different acidity soils, which will reduce the half-life of pesticides and thereby reduce environmental damage to humans.

The results of this work can be used in planning and calculating the introduction of pesticides in various crops.

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