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ANALYSIS OF THE STATE OF ORGANOCHLORINE PESTICIDES USE AND THEIR IMPACT ON THE ENVIRONMENT AND LIVING ORGANISMS

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Abstract

Ecological features of the organochlorine pesticides use in agriculture are investigated in the paper. In addition, general characteristics of the pesticide preparations found in Ukraine and specific features of the organochlorine pesticides have been analyzed. The toxicological effect of organochlorine pesticides on humans and other living organisms and technology of their application in agriculture have been examined.

The review of hygienic indicators of pesticides rationing is carried out in the work.

Ways to reduce pesticide environmental pollution are considered. The basic directions of their application, which allow to minimize toxic loading on the environment are offered. Methods of neutralization of unusable pesticides are considered. Among the various techniques of disposal, recycling and recovery of toxic waste, which are used today, three main groups are distinguished: thermal, chemical and biological methods.

Keywords: pesticides, toxic waste, rationing, maximum permissible concentration, lethal dose, insecticides, fungicides.

Introduction. On the territory of Ukraine, a significant quantity of inapplicable and banned pesticides of the category «A» (prohibited), «B» (unusable), «C» (unidentified) has been accumulated. The final amount is not established, despite repeated attempts to conduct a comprehensive state inventory, what indicates a negative status of their recording and storage. The current state of storage of pesticides has affected the multiple exaggeration of their maximum permissible concentration (MPC) in the soils of a number of regions of Ukraine.

This, in turn, contributes to the increase in the incidence rate of the population of Ukraine, which is characterized by regional differentiation. It is associated with the general environmental pollution, in which the pesticide component has a significant share. Recently, there has been a significant increase in the number of diseases in different parts of the country. Thus, these data suggest that pesticides of category «A», «B» and «C» can be considered highly toxic substances of slow action against living systems.

Meanwhile, in the world practice there are neither specially developed accepted methods of the banned pesticides disposal, nor the scientific methodology or basic technologies developments for doing such work. As a rule, utilization is reduced to their incineration, containerization or burial on the specially designated sites. The possibility of effective use of the eleminated active substances of pesticides in various industries has determined the development of reagent methods for the removal of unusable organochlorine pesticides.

The purpose and objectives of the study. The aim of the work is to determine the number of unusable organochlorine pesticides and methods of their neutralization. To achieve this goal it is necessary to solve the following tasks:

- analyze the current state of storage, technical processing and disposal of pesticides, including unusable ones;
- characterize the toxic effect of pesticides on the environmental medium and living organisms;
- substantiate ways to reduce the toxic effects of pesticides on the environment and living systems.

The object of the research is the process of the organochlorine pesticides toxity elimination.

Materials and methods of research. Theoretical studies of the basic laws of the organochlorine pesticides reagent treatment are executed on the basis of provisions of the general organic substances chemical technology. The operational characteristics of various technical mixtures, which included organochlorine pes-

ticides (OCP) in their possible reuse in technical facilities, were determined according to the current methods of the State Standard of Ukraine.

Results and discussion. One of the main types of pesticides used in agriculture is organochlorine ones. They are used as herbicides, insecticides, acaricides and fungicides.

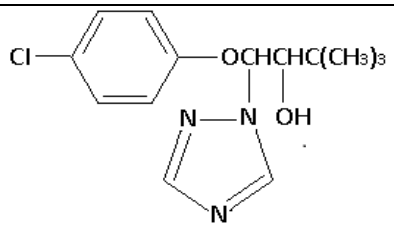
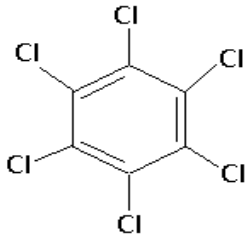
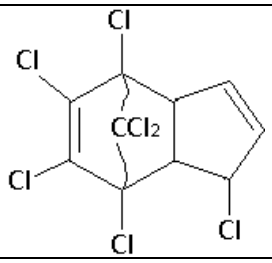
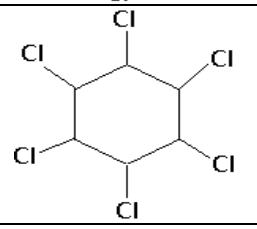
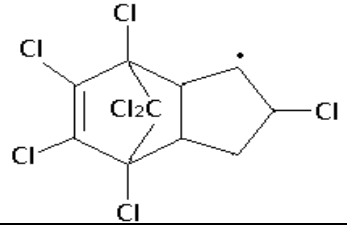
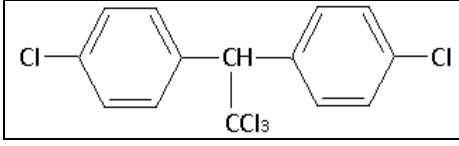
These preparations are the chlorine-derived multinuclear carbohydrates, cycloparaffins, compounds of the new series of terpenes, benzene and others. Most of the organochlorine pesticides are poorly soluble in water, but well soluble in organic solvents [4].

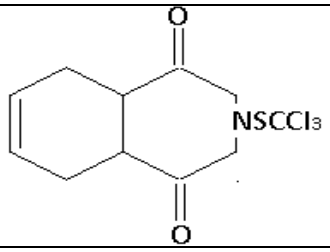
A special property that distinguishes these pesticides from other ones is their resistance to temperature, insolation, moisture and other environmental factors. As to the hygienic classification, many organochlorine pesticides (OCP) are highly resistant pesticides. For example, DDT is fixed in the soil for 8-12 years after its use, heptachlor is found in 4-12 years after application.

A specific feature of the organochlorine pesticides is their concentration increase in the biological chain, i.e., their cumulative ability. OCPs are accumulated in plant and animal products. Toxic chemicals can enter the body of animals and birds during their skin treatment, through the digestive system, as well as a result of the direct introduction of the drug into the stomach to fight parasites. Table 1 presents chemical formulas, active substances, melting point and toxicological index of each preparation of the OCP class.

Table 1

Some of the organochlorine pesticide preparations

Formula	Name	Melting point, ºC	LD_{50} for laboratory rats, mg/kg
	Baitan	112	363-568
	Benzachlor	231	1700-4000
	Heptachlor	95	500
	Hexachlorocyclohexane	309	300-500
	Dilor	130	> 2000
	DDT	109	1455-1750

	Captan	172	9000-12500

Depending on the toxicity of organochlorine pesticides, the maximum permissible levels (MPL) of the pesticide content in the products and the maximum permissible concentration (MPC) are defined. The data for each preparation are presented in tables 2 and 3.

Table 2

Maximum permissible levels of some OCPs in products, mg/kg

Pesticide	Product	Maximum permissible level, mg/kg
Hexachlorbenzene	wheat grain	0,01
Heptachlor	–	not allowed
Hexachlorocyclohexane	potatoes	0,1
	cereals	0,2
	fish	0,2
	milk	0,05
Dilor	grape	0,2
	sugar beet	0,2
DDT	potatoes	0,1
	meat	0,1
	sugar	0,005
Captan	food products	0,35
	berries	not allowed

Table 3

Maximum permissible concentration of OCPs in natural environment objects

Pesticide	Maximum permissible concentration	
	Water objects, mg/l	air, mg/m^3
Hexachlorbenzene	0,05	–
Heptachlor	0,05	0,0002
Hexachlorocyclohexane	0,02	–
Dilor	0,1	–
DDT	0,1	0,001
Captan	2	0,01

Pesticides not only act as harmful substances, but also have a negative effect on the environment components. First of all, the soil suffers from the pesticides use. Many of the toxic substances can remain unchained in the soil layers for a long time, causing the following negative consequences: inhibit biological activity; resist natural restoration of soil fertility; cause loss of nutritional value and taste qualities of agricultural products; reduce the yield of many crops due to the death of pollinating insects; run down humus reserves in the soil; increase products losses and shorten their shelf life. A small proportion of organochlorine pesticides gets into the atmosphere. Quite a large amount of these substances enters the soil layer, then, during the evaporation process at higher temperatures rises to the upper atmosphere. There they mix with air masses and move over long distances. After precipitation, pesticide impurities together with rainwater get not only into soils in the fields, gardens or orchards, but also in places that are not used by humans [5, 6].

As has been already mentioned, pesticides are able to affect not only the components of inanimate nature, but also bioorganisms.

For example, toxic chemicals can adversely affect the nature of interaction between plants and microorganisms, especially those in symbiosis. The main role in decomposition of those substances belongs to the micro-fauna and enzymes produced. But, when pesticides get into the soil, there arises unforeseen problems with decomposing of these compounds. As a result, the air exchange regime, dynamics and nature of distribution of chemicals by the soil profile change greatly. All this in some way affects the formation and activity of the microbiota [5].

The interaction of pesticides with microorganisms depends on many factors, especially on the chemical and toxicological properties of the active substance. In particular, some pesticides (including organochlorine preparations) block nitrification processes, what leads to ammonium magnification in the soil. As a result, nitrogen losses are reduced and the release of its volatile oxides shortens. The effect of pesticides in this case is

positively evaluated. But if the chemicals inhibit nitrogen fixation, this causes negative consequences.

Microorganisms decompose almost all currently existing pesticides, even as resistant as DDT and its analogues. Therefore, the stability of pesticides content in natural surrounding is conditioned by the lack of microfauna or unsuitable conditions, which hinder its ability to fulfill this task. And these indicators in turn are to some extent influenced by the pesticides application [2, 4, 7].

As to the other living organisms, pesticides affect them quite indirectly. Initially, the substance after entering the upper fertile layer is broken down and partially absorbed by plant organisms. These compounds then are stored in plant tissues. After grazing by the animals, pesticides together with the feed mass enter the animal body. There they, migrating throughout the body, lead to various organs pathologies, depending on the amount of the active substance and the degree of accumulation. It is difficult to remove pesticides from the body. Quite often fatalities due to animals poisoning with pesticides can be observed.

Scientists had developed technologies for the disposal of unusable pesticides and other toxic chemicals aggregated at agricultural enterprises, which have long been waiting to be implemented. The problem of safe storage and elimination of the non-certified dead stock of those substances needs immediate solution.

For instance, in Vinnytsia region, more than 2,000 tons of unusable, unrecognizable and substandard pesticides, remained on farms since the times of the USSR, among which there are organochlorine class pesticides, have been stored in 400 warehouses. More than 50 of those storage structures are in neglected condition and require urgent reclamation. Many of them do not have roofs. Precipitation falls on the chemicals and they are spread over large areas by the groundwater. As a result, there is an increase in morbidity, mortality, and a decrease in the birth rate in the region [5]. Similar processes are taking place throughout the state. Today in Ukraine, according to official statistics, more than 200 thousand tons of toxic pesticides are being stored. But this figure is rather virtual. For example, in Dnipropetrovsk region, in Zhovti Vody alone, 20,000 tons of pesticides are buried. But for some reason they are not reflected in official documents.

Introduction of chlorine into organic compound gives it biological activity, which is manifested in the important biological processes in microorganisms, plants and animals blocking, including photosynthesis, cell fission, affect respiration of plants and animals, etc. Due to these properties, biologically active chlorine-containing organic compounds are used for the manufacture of pesticides in order to control harmful and unwanted microorganisms, insects and fungal diseases.

During their storage, especially in open areas, pesticides get into the river, ground and subsoil waters. Currently, various methods have been developed for the disposal of unusable pesticide remainders. Among the various methods of disposal, utilization and burial of toxic waste used, three main groups can be singled out. They include thermal, chemical and biological methods.

The thermal method is considered to be traditional, is widely used and meets sanitary requirements, i.e. the final content of harmful impurities after thermal disposal does not exceed the maximum allowable concentrations. One of the most common types of thermal method is the destruction of pesticides by incineration using natural gas. It is known that this process is used for deactivation of many phosphorus and chlorine-containing chemicals. Its advantage is in maintaining a constant sufficiently high temperature, which guarantees complete decomposition and combustion. Method of pesticides incineration in furnaces specially designed for this purpose, equipped with hazardous substances removal systems and other modern tools is recognized and used worldwide [4, 6].

Chemical or reagent method of pesticides disposal is used for water bodies disinfection, for the disposal of unusable pesticide residual stocks. The essence of this method is that various reagents are added to the preparative mixture of pesticides, such as alkaline components, which are able to react with the contaminants, forming secondary insoluble compounds used in industry. For example, by-products of an organochlorine pesticide such as 2,4-D amine salt can be used as additives to industrial oils used in various technical processes and corrosion inhibitors [2].

The reagent method of processing unusable pesticides, unlike others, does not require any large equipment costs. Mixing of preparations with reagents can be carried out in ordinary metal barrels or special equipment according to the corresponding technological patterns. The warehouse itself can serve as the premises for this process. The reagent method of processing unusable pesticides has its peculiarity: it is advisable to use it for the disposal of pesticides with more than 50% content of active substance. Thus, before choosing the method of disposal, it is necessary to first establish the content of the active substance in the toxic chemical, which is in organochlorine pesticide is determined by the method of potentiometric titration. The analyses can be carried out either at the place of the pesticide disposal in the presence of the necessary equipment and reagents, or in a special research laboratory [2].

Figures 1 and 2 demonstrate technological schemes for the reagent treatment of some organochlorine pesticides [8].

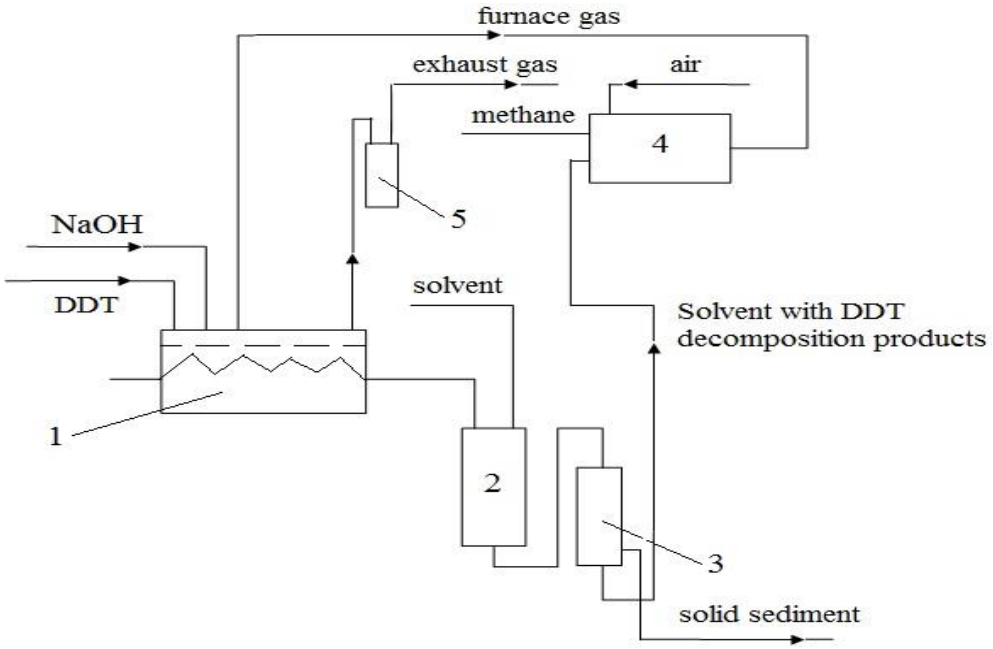


Figure 1. Technological scheme of reagent treatment of DDT: 1 – reactor with the auger; 2 – reactor; 3 – centrifuge; 4 – organic solvents combustion chamber; 5 – bubbling machine

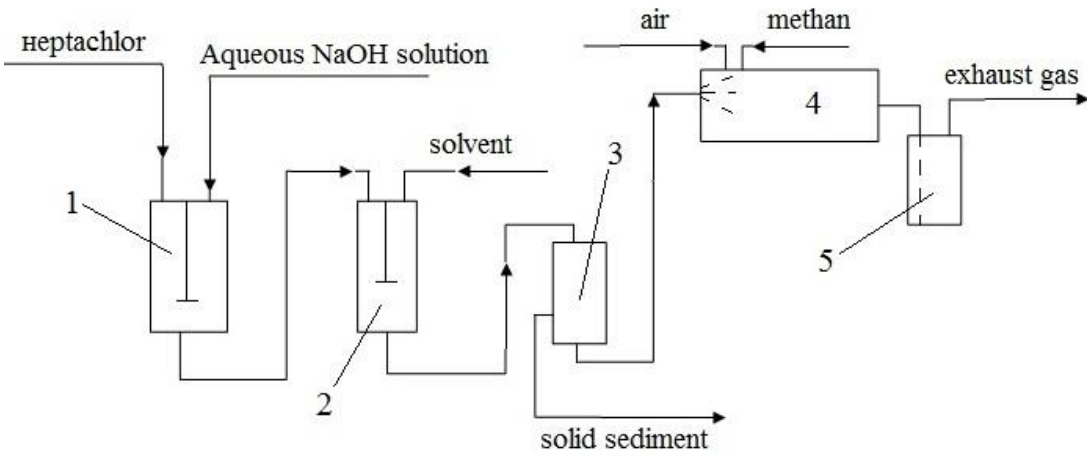


Figure 2. Technological scheme of reagent processing of heptachlor: 1 reactor no. 1; 2 – reactor no. 2; 3 – centrifuge; 4 – organic solvents combustion chamber; 5 – bubble column

The essence of biological methods of disposal is the use of microorganisms. That is, it involves the disposal of prohibited and unusable chemicals by way of their natural decomposition in organosoil composts with the subsequent production of organic matter. Microbiological composting may be carried out, algae or other higher aquatic organisms are used as well. Microorganisms are able not only to maintain soil fertility, but also to contribute to degradation of pesticides. Biological disposal methods are considered to be the most environmentally friendly.

Besides, pesticides themselves are able to decompose under the action of various environmental factors [7, 2].

It is entirely possible that during storage and use of pesticides, the territory contamination can occur. Areas of land contaminated with pesticides are disinfected with chlorinated lime and dug up. Dust collected from the overalls, wastewater formed, containers, transport, premises should be also treated with chlorinated lime during the day. To prevent contamination of soil, water bodies, atmosphere and air of the area of operation, industrial and domestic wastes generated in greenhouses, waste soil, mineralized substrate and plant residues must be neutralized. Drainage effluents in conditions of application of pesticides of any class in greenhouses before their canalization are to be subjected to preliminary treatment (neutralization). The most promising methods of purification them from pesticides are UV irradiation together with electrocoagulation and electroactivation treatment.

A special problem is also a complete disposal of the toxic chemical preparations. To do this, it is necessary to separate non-combustible fillers and additives from combustible organic biologically active compounds. This separation can be accomplished by extraction of the biologically active compound with the use of organic solvents. Therefore, it is necessary to take an appropriate solvent for this task [8].

Thus, now there exist a large number of methods for unusable pesticides recovery, available for practical

application. And in the current environmental situation, this issue is one of the most urgent and important.

Conclusions.

1. Analysis of the current state of pesticides storage and their impact on the environment and living systems has been carried out. Organochlorine pesticides have been found to be the heaviest toxic substances, requiring immediate recovery and disposal.

2. The rates and maximum permissible concentration of organochlorine pesticides in the soil, water and atmospheric air are scientifically substantiated, which allowed evaluation of their ecotoxicological effect on living systems.

3. Ways to reduce the impact of the toxic pesticides on the environment, sanitary requirements for their disposal and utilization, as well as features of labor protection and safe handling of these substances have been considered. Environmental and economic efficiency of introduction of the reagent processing of unusable pesticides method, which makes it possible to increase the environmental security of the region and solve important scientific and economic problem has been substantiated.

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ПРАКТИЧЕСКИЙ АНАЛИЗ ПЛОДОНОШЕНИЯ ЧЕРНИКИ В ЛЕСАХ ГОРОДА СОКОЛ ВОЛОГОДСКОЙ ОБЛАСТИ

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