Abstract. In Ukraine, there is still a great number of unused, unidentified and substandard pesticide preparations (PPs) and other toxic substances which have an extremely dangerous impact on humans and other living ecosystems and the environment. Besides, more than 75 thousand tons of pesticides are imported and produced annually in Ukraine, but some of them are not used during the period of their suitability. Consequently, when stored mostly in dilapidated warehouses and repositories of agrochemicals, as well as in the open areas, they fall into underground and ground water, and then through trophic chains into the organisms of living systems, causing severe poisoning and diseases. We note that till now, the problem of unsuitable PPs was solved only in the context of their utilization or export for processing outside the state, while the rest of this ecological problem – the restoration of soils and the remediation of contaminated lands at the state level, is not virtually solved. Therefore, the substantiation of the scientific and practical aspects of environmental safety management of such remediation processes is on time.

Key words: environmental safety, substandard pesticides, contaminated soils, warehouses and repositories of pesticides, restoration, remediation, reclamation, ecological risks.

1. Introduction

The dilapidated warehouses and storage repositories of agrochemicals containing residues of unsuitable pesticides and other toxicants that under the influence of external factors were transformed into unidentified toxic mixtures are an extremely acute environmental problem. Territories and soils around the repositories of toxic chemicals are heavily contaminated with leaky PPs. This is, as a rule, the territory adjacent to the warehouse of pesticides and mineral fertilizers within a radius of up to 500 meters, which was not taken care of by anyone, and until recently, almost in most cases was unproductive. In this case, adjacent territories together with the repository of chemicals can range from 0.5 to 8–10 hectares of fertile land. Considering that there are several thousand of such warehouses in Ukraine, it is possible to estimate approximately the extent of environmental disaster, which is more than 10 000 hectares, that is, about 0.02 % of the total area of the state [1–20].

2. Results of the research

Analysis of methods of the restoration of pesticide-contaminated soils.

We have investigated on the example of a separate warehouse of pesticides near the village of Vinnitski Khutory near Vinnytsia, that the excess of concentration of some pesticides stored there is noted at a distance of up to 500 meters and up to 6 meters deep, that is, the two-vector nature of migration (vertical and horizontal) [1, 12, 14].

At present, most warehouses are already cleared from obsolete, substandard and prohibited pesticides and
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fertilizers, which are mainly brought to the basic warehouses, but the buildings themselves, which need either restoration or demolition, remained and have a detrimental effect on men and the environment, aesthetic as well as toxic.

At present, there are many engineering and technological methods and ways of soil restoration from various contaminations. However, the technologies for cleaning the land contaminated with pesticides with multiple excessive MACs are imperfect, costly and complex.

Table 1

Methods of the restoration of pesticide-contaminated soils. Advantages and disadvantages

| No | Methods                                                                 | Advantages                                      | Disadvantages                                                                 |
|----|--------------------------------------------------------------------------|-------------------------------------------------|-------------------------------------------------------------------------------|
| 1  | Excavation with further immobilization or bioremediation                 | – a very easy way                               | – costly;                                                                     |
|    |                                                                          |                                                 | – can be applied only to small areas, for example, in the areas of technical disaster |
| 2  | Water pumping and treatment of contaminated solutions                    | – highly reduces the high concentrations of pollutants | – non-aqueous phases present in soil solutions;                               |
|    |                                                                          |                                                 | – unknown geology of the underground space                                   |
| 3  | Soil steam extraction                                                    | – minimum soil violation; – a short-term process, low cost | – can be applied only to the unsaturated zone;                               |
|    |                                                                          |                                                 | – does not distribute dioxins, polychlorinated biphenyls; – possible emissions of pollutants into the atmosphere |
| 4  | Injection (supply of spray air or oxygen) to accelerate the biodegradation of pesticides | – non-destructiveness of the method, - reasonable cost, - perfect equipment | – the presence of numerous channels through which the air diffuses to the surface; |
|    |                                                                          |                                                 | – the presence of solid zones with low permeability                         |
| 5  | Heating of the polluted zone by electric current or radio frequency field (thermal methods) | – applied for any type of soil, heated soil for a long time promotes bioremediation | – small size plot; – petroleum products and lubricants hamper the process of remediation; – the presence of metal structures creates the paths of current and electrical safety |
| 6  | Electrokinetic methods (electroosmosis, electrophoresis, electrolysis)   | – high efficiency- many different pollutants can be removed | – the presence of significant constant currents; – the need for special membranes; – insignificant areas; – the need for large inert electrodes |
| 7  | Bioremediation                                                           | – sufficiently effective for the purification of soil and groundwater | -necessity of application of special microorganisms                           |
| 8  | Plowing                                                                  | – successfully used to remove residues of petroleum products, hydrocarbons and pesticides; – acceleration of microbial degradation of hazardous components; – simplicity | – requires large areas; – a long-term process; – inorganic compounds (eg. mineral fertilizers) are not subject to bioremediation |
| 9  | Composting and biofeeding                                                | – simplicity; – short-term action; – low cost; – requires less space than plowing: | – formation of unpleasant smells; – the presence of large concentrations of heavy metals suppresses the growth of microflora |
| 10 | Fitomelioration                                                          | – simplicity; – immutability of the landscape; – aesthetic appeal | – need for recycling of contaminated biomass                                   |
Organization of work on the restoration or demolition of structures of warehouses and equipment.

To work with buildings and equipment, it is necessary to conduct a preparatory stage during which to estimate the scope and volume of work, to calculate the ecological and economic feasibility of restoration or demolition of the warehouse, to provide access roads, etc. At the same time, if the repository (warehouse) is not reinstated, then it must be demolished with the obligatory cleaning of the structural elements of the building and the soil under it from the residues of pesticides. It is recommended to clean the warehouse areas in several stages:

- dismantling and removal of construction residues on crushing industrial sites;
- if a repeated excess of MAC in the soil is detected, then asphalt, concrete, slabs, and soil are completely removed;
- leveling of the territory;
- cleaning of soil cover from residues of pesticides by one of the above methods. This is done in special containers filled with washing or detoxifying agents, such as lime solutions.

To increase the reliability of the insulation of surfaces and materials contaminated with pesticides should be further processed, for example, by a mixture of liquid glass and quenched lime. Exhausted solutions of detergents are also cleaned in special equipment, which makes it possible to neutralize them.

The cardinal method of purifying the seeds of crushed structures that are contaminated with pesticides can be a thermal one. Also, instead of the soil which is removed from the place of the demolished warehouse, the humus layer is brought in and leveled. After that, work is done on the reclamation and remediation of the territory with the corresponding restoration of natural land resources, biogeocenoses, preservation of landscape and species diversity and ensuring ecological balance in nature. Therefore, the ecological, economic and social effects of such recovery operations can be: restoration of the natural environment, improvement of the environment, creation of favourable living conditions for the population, reduction of the risk of diseases and poisoning, as well as increasing the ecological safety of the region (Fig. 1).

Assessment of ecological risk from contamination of soils and territories of warehouses.

To establish the expediency of introducing appropriate methods of soil restoration, it is necessary to assess the level of environmental risk from contamination with pesticides and other toxicants. Ecological risk is the probability of occurrence of dangerous (unfavorable) for the environment and living systems of consequences or influences, or events and corresponding losses. At the same time, it is difficult to completely exclude ecological danger, but it is quite realistic to minimize the probability of risk. Therefore, the model of the situational risk from the use of pesticides can be represented as follows:

\[
R = \frac{1}{2I_{SC}} \sum [A_i + B_i + D_i],
\]

where \(I_{SC}\) is the self-cleaning index of soils of this area; \(A_i\) is the impact (load) of the \(i\)-th pollutant on a person; \(B_i\) is impact (load) of the \(i\)-th contaminant on the MPC on the natural environment; \(D_i\) is the impact (load) of the \(i\)-th contaminant on the population, for example, from the use of products grown on the pesticide-
contaminated area and epidemiological contacts of people with pesticides.

In this case, the self-cleaning index of soils is determined depending on the zone of possible application, toxic and hygienic properties of the pesticide, the volume of its use, etc. For example, for the Vinnytsia region, the average value of the self-purification index is \( I_{gc} = 0.61 \). Load levels (effects) \( A, B, D \) – are defined as the ratio of the mass of the active substance to the area of the contaminated area, the mass of the human body and the integral evaluation of the epidocontact, respectively [14,15]. It has been proved that all types of pesticides cause various pathologies in human body systems and other living objects, and in the vicinity of the territories of warehouses of pesticides, the morbidity of the population is significantly higher compared to other regions and cities where people are less exposed to pesticides and agricultural production.

Consequently, as our analytical risk assessment suggests, for example, on the warehouse of toxic chemicals in the village of Vinnytsia Khutory, the total absolute risk value is more than 5–10 times compared to the similar data for non-contact areas. This convincingly confirms the urgent need for agrotechnological and bioremediation measures for soil clearing on the territories of existing and former warehouses of pesticides.

Conclusions

Consequently, in modern conditions of increased use of plant protection chemicals and catastrophic contamination of agro-ecosystems with pesticides from local sources (in particular, warehouses and repositories of toxic chemicals) it is relevant to select and apply optimal methods for restoration of the respective territories. In addition, thorough assessment of environmental risks is a prerequisite for re-planning and restoration work, which will make it possible to predict and significantly reduce potential harmful consequences for the environment and people, as well as effectively manage the environmental safety of storage sites and handling of toxic chemicals.

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