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ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ**

# БАЯНДАМАЛАРЫ

# ДОКЛАДЫ

**НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН**

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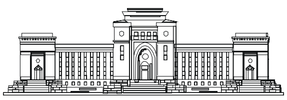

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ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ
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# POP PESTICIDES AND RECLAMATION METHODS (REVIEW)

**Abstract.** A thorough analysis of the foci of pollution with POPs pesticides and the development of methods for the remediation of contaminated areas is one of the key areas of the Kazakhstan Republic strategic development plan. The huge production of POPs pesticides, their over-purchasing by agro-industrial companies, as well as changes in agricultural infrastructure related to the liquidation of collective farms, state farms and land privatization led to their accumulation in warehouses in many CIS countries, including the Republic. When they getinto the environment with rain, wind, as a result of floods, landslides and fires, they pose an environmental hazard to human health and the environment, both locally and globally. In this regard, the article presents a literature review on the problems of POPs pesticides and methods for their reclamation. Modern methods of obsolete pesticides disposal (isolation, burial, immobilization, soil washing, electro-reclamation, heat treatment, etc.) and methods of pesticide-contaminated lands reclamation (bioremediation, phytoremediation, and vermiremediation) are considered. Particular emphasis was placed on phytoremediation technologies for POP pesticides in soil and methods for increasing their effectiveness, since this technology is an economically viable and environmentally friendly technology. The conditions for optimizing the environment using chemicals (low molecular weight compounds, carbon materials (biochar) and nanomaterials) and plant-microbial associations to stimulate the development of the plant organism increase the phytoavailability of POPs pesticides and increase their mobility in soil and water systems are considered in detail.

**Key words:** POP-pesticides, reclamation, phytoremediation, optimization, environment.

## Introduction

Persistent organic pollutants (POPs) are organic compounds of natural or anthropogenic origin, which have a special combination of physical and chemical properties, so that after they enter the environment they do not decompose for long periods of time, because they are highly resistant to photolytic, chemical and biological degradation [1]. POPs are classified into four categories: low mobility POPs; relatively low mobility POPs; relatively high mobility POPs and high mobility POPs (Table 1). The classification is based on three characteristics: vapour pressure of a supercooled liquid at 25°C; octanol-air partition coefficient; the temperature of condensation. Low mobility POPs precipitate and are held close to the source, while high mobility POPs undergo atmospheric dispersion throughout the globe without precipitation [2;3]. POP's can fractionate as they move to the poles because they migrate at different velocities [3].

Most POPs are mobility enough to vaporize and precipitate in air, water and soil at ordinary ambient temperatures. Warm temperatures (tropical areas) promote a potential for atmospheric dispersion of POPs due to increased mobility and rate of degradation than in temperate climates.For the first time in 1974, scientists suggested the possibility of the migration of POPs in the atmosphere in the form of gases, aerosols and condense in areas with low temperature [4].Natural decomposition reactions also slowdown in the cold, allowing POPs to remain intact for longer and become more resistant. Cases of detection the POPs in the tissues of Arctic animals and marine habitats have been regularly recorded since the late 1960s, becoming more frequent by now [5-8].

Table 1 –POP pesticides classification [3]

| Low mobility | Relatively low mobility | Relatively high mobility | High mobility |
|---|---|---|---|
| Location | | | |
| Fast deposition and retention near the source | Preferential deposition and accumulation in the middle latitudes | Preferential deposition and accumulation in polar latitudes | Atmospheric dispersion in the world, no deposition |
| Temperature | | | |
| > +30°C | from+30°Cto -10°C | from -10°C to -50°C | < -50°C |
| Chlorobenzenes | | | |
| - | - | 5-6 Cl | 0-4 Cl |
| PCBs | | | |
| 8-9 Cl | 4-8 Cl | 1-4 Cl | 0-1 Cl |
| PCDDs | | | |
| 4-8 Cl | 2-4 Cl | 0-1 Cl | - |
| PAHs | | | |
| > 4 rings | 4 rings | 3 rings | 2rings |
| POPs | | | |
| Chlordecones (Mirex & Kelevan), benzo[α]pyrene | DDT and its analogues (Metoxychlor & Dicofol), Cyclodienes (Endosulfan, Aldrin, Dieldrin, Chlordane, Heptachlor, Isobenzan) | HCB, HCH and its isomers | Napthalene |

Studies by Russian scientists have established that pesticides are present in the Arctic region [9], and that significant volumes of pesticides (for example, hexachlorocyclohexanes, DDT, chlorobenzenes) are transported to the Arctic by the rivers. In 2002, more detailed information was published from Russian regions, including on the concentration of DDT and toxaphene in the Kara Sea and the surrounding areas, based on which it can be concluded about the continued use of DDT and toxaphene, and (or) leaks from old storage facilities. In 1997, the AMAP working group presented evidence of high pesticides in animals in the Arctic. In the Arctic regions, many air and water transport routes end, so large volumes of persistent pesticides and other pollutants accumulate in them. In the Arctic region, the destruction of pesticides is slow due to low temperatures and, therefore, pesticide residues remain in the environment for a very long time after their planned use.

The biomagnification of POP's is one of the most pressing issues, the deposition of persistent organic compounds on the links of the trophic chain occurs mainly in the liver and adipose tissue, due to the lipophilic nature of pesticides.The first public warnings of potential POP's hazards were related to local environmental impacts in the early 1960sand intensified in the 1970s [10]. POPs have been found in various human matrices, including blood, breast milk and placentain the 1970s. It is known that human health problems, such as endocrine disruptions, cancer, reproductive disorders, cardiovascular diseases and immune system problems are caused or exacerbated by these compounds due to constant exposure and accumulation [11]. Currently, one of the most serious health problems of POPs is their carcinogenic effects. The greatest impact occurs mainly with the use of contaminated agricultural products containing pesticides or their metabolites [12]. Being bioaccumulative POPs even in very low concentrations can cause several generally insignificant effects on human health, fish and wildlife along the food chain [11].

Due to the danger of POPs, the Stockholm Convention on Persistent Organic Pollutants was adopted in 2001and entered into force in 2004. Parties to the Convention have committed to reduce the amount of POPs that could have a negative impact on humans and travel over long distances. The Republic of Kazakhstan signed the Stockholm Convention on POPs on May 23, 2001 and ratified it on June 7, 2007, thereby committing itself to not producing, not using and destroying stockpiles of chemicals recognized as especially life threatening. The jurisdiction of the convention included 12 chemicals, including nine pesticides, namely DDT, aldrin, dieldrin, endrin, chlordane, heptachlor, mirex, toxaphene and hexachlorobenzene. However, the list of POPs is constantly updated with new substances. At the fourth meeting of the Parties Conference, held in 2009, an additional five pesticides (chlordecane, alpha hexachlorocyclohexane, beta hexachlorocyclohexane, lindane, and pentachlorobenzene) and four industrial chemicals (octabromodiphenyl ether, pentabromodiphenyl ether, perfluorooctane sulfonic acid, and perfluorooctane sulfonyl fluoride) were included. In 2015, brominated flame-retardants (PBDEs, HBCD and HBB) and PFOS and related precursors as first perfluorinated-alkylated substances (PFASs) were included in the list as well [13]. Thus, as of 2013, the list of POPs included 13 items of organochlorine pesticides.Due to Stockholm Convention the POPs have to be destroyed and liquidated [14].

The production and use of POP-pesticides in developed countries, including Kazakhstan is prohibited or restricted. However, widespread production, large purchases of pesticide products by governments, poor stockpile management, and reluctance to make changes and their use after the ban led to their accumulation. They become obsolete and undesirable when they can no longer be used for their intended purpose because they are prohibited [15].Tons of obsolete and undesirable pesticides are accumulating worldwide. A significant amount of these pesticides is included in the POPs group and is of particular concern because of their toxicity, persistence, long-distance transmission and accumulation in the fatty tissues of humans and animals [16]. Obsolete stocks of pesticides not only pose a threat to public health and the environment, but can also pollute natural resources and inhibit socio-economic development [11].Although these prohibitions and restrictions were introduced during the 1970s and 1980s, some countries (India, Africa, South America etc.) still use and produce POP-pesticides for agriculture because of their low cost and versatility in controlling various pests[17].

Unfortunately, so far little attention has been paid to environmental safety at the state level, even though many countries have ratified the Stockholm Convention. According to the “International HCH & Pesticides Association”, the exact number of obsolete pesticides in the countries of the former Soviet Union, including Kazakhstan, has not been established and varies widely[13].

According to UNEP [18], because of an inventory of obsolete pesticides in the country, more than 1500 tons of banned, unsuitable for use pesticides and their mixtures of unknown composition were registered. The data of 2008 indicate that their number reached 10000 tons. The Department of Environmental Protection of the Almaty region believes that 87 tons of obsolete pesticides should be disposed of, whereas, according to the Ministry of Agriculture, only 126 tons should be destroyed. According to the Ministry of Agriculture (as of July 2012), Kazakhstan has 22 typical warehouses that store 2231 tons of pesticides; 580 adapted warehouses in which 17049 tons of pesticides are stored. There are 392 operating warehouses in the Republic (the largest number of warehouses is in the Akmola region – 224, and in the East Kazakhstan region – 68). The largest capacity warehouse (for storage of 4700 tons of pesticides) is located in the Shortandy district of the Akmola region. In total, about 6931 tons of obsolete, banned and unusable pesticides are stored in warehouses of various regions [19]. Due to the lack of a full-scale inventory in the Republic of Kazakhstan, the data on the number of the former storehouses, as well as the quantity and quality of obsolete pesticides, are contradictory,that evidenced an imperfect management system and that caused a serious danger for environment and human health[20]. In this regard, the restoration of contaminated soil is one of the priority areas in all regions of the world, because it has social and economic value for restoring soil health and increasing its productivity. The search and use of inexpensive recovery methods that can be implemented by farmers with limited equipment and experience are of great importance.

**Remediation (Reclamation) of POP-pesticides**

*Ex situ,*physical and chemical methods are traditional approaches to the remediation of contaminated POPs of soils[21, 22].

***Physical methods of remediation***:

*insulation* – pesticides are isolated and held by physical barriers, which are used in the manufacture of steel, concrete, bentonite, clay and tile walls;

*separation of pesticides from the soil*–for separation of pesticides from the soil there are used high frequency heating, electrokinetic processing and soil flushing. After excavation,there are used soil-flushing, extraction by solvent and thermal desorption. Insecticide DDT is successfully removed from contaminated soil under thermal desorption at 450-500°C.

*burial* – removal of contaminated soil from the contaminated site and pollutants in a special site for backfilling and restoration of the site, which may include backfilling the dug space with clean soil with the subsequent creation of vegetation;

*stabilization/immobilization*– mixing contaminated soils with hardening materials, such as cement or other pozzolanic materials, such as siliceous or aluminous materials with cementing properties, or thermoplastics or other suitable agents;

*soil washing*– particle separation method by washing process and the leaching technique using chemical extractants;

*electro-reclamation*– based on the electrokinetic process that occurs during the flow of direct current between the cathode and anode inserted into the soil. This method is most successfully applied on highly clay soils containing organic or relatively mobile pesticides;

*heat treatment*– removal of organic contaminants by chemical degradation and volatilization by heating the soil to high temperatures by heating by electrical resistance, radiofrequency/electromagnetic heating, injection of hot air/steam.

*hyperthermal combustion of pesticides wastes*–liquidation the stokes of obsolete and undesirable POP-pesticides is combustion in specialized high-temperature combustor. The optimal conditions for destroying the POP-pesticides in combustors are 1000°C and period for 2 seconds. Such equipment is on the restricted amount in developed countries (for example, Czech Republic), but this method is not available for developing countries due to their absence. Cement ovens, that are present in developing countries, can be used for combustion the obsolete pesticides stokes, but this approach led to air contamination by toxic substances (furans, dioxides, etc.).

***Chemical methods of remediation***– treatment of the contaminated soil by KOH, mixes of Ferrum, Aluminium sulfate and vinegar acid. Decay effectiveness of pesticides is 99%; this method is suitable for developing countries.

These technologies are successfully used in developed countries of the world, but they are extremely energy-intensive and require large investments. The burial of POPs in repositories also requires significant financial costs, also, pollutants for many years in the open air were absorbed in high concentrations in the soil and, therefore, it is necessary to remove not only xenobiotics themselves, but also huge volumes of soil. Besides, they are not environmentally friendly.An alternative to traditional technologies is successfully used innovative technologies: bioremediation and phytoremediation.

***Biological methods of remediation***involves various methods, such as biode-gradation using microorganisms in the soil, phytoremediation using plants, or vermi-remediation using earthworms.

*Bioremediation.*Bioremediation agents are bacteria and fungi that use pollutants as a source of nutrients or energy. The microbial diversity of the site is one of the most important parameters of bioremediation, along with the nature of pollutants and some soil properties (pH, moisture content, nutritional status, temperature, redox potential). Bioremediation has been successfully used for the degradation of pesticides, such as lindane, atrazine, diuron, erbutosaline, metalaxyl, DDT, gamma-hexachlorocyclohexane (γ-HCH), dieldrin, aldrin, heptachlor, chlordane, lindane, and lichen*Trametes*, valued at \$80 and \$120 per ton[23].One of the most important reasons for using bioremediation to eliminate organic pollutants is that bioremediation is a cost-effective and environmentally friendly method that makes it possible to destroy or neutralize organic pollutants using natural biological activity.

Bioremediation consist from bio-augmentation, biostimulation and composting.

*Bio-augmentation* is the process of inoculation of enriched/acclimatized consortia or strains that decompose individual pollutants. The biodegradation of chlorpyrifos was studied in the mineral medium and soil using a new strain of fungi *JAS1*isolated from rice field soil [24].

*Biostimulation* - the addition of appropriate nutrients (nitrogen, phosphorus, trace elements) to provide microorganisms with an environment that contributes to the development of metabolic pathways for biodegradation of pollutants. In their study, I. Ortíz [25]and colleagues proved that stimulating the local microbial flora of the soil by adding small amounts of secondary carbon sources enhances the biodegradation/mineralization of DDT and its main metabolites.

*Composting* - mixing contaminated soil with non-hazardous organic additives (e.g., manure, agricultural waste) suitable for composting, to stimulate the develop-ment of bacteria or other organisms populations, such as fungi, earthworms, etc., that can decompose pollutants in the soil through co-metabolic pathways. T.B.Moorman with colleagues [26] used several organic modifications, including compost, a by-product of corn fermentation, corn stalks, manure, peat, and sawdust to improve the removal of toxic pesticides (atrazine, trifluralin, and metolachlor) from contaminated soils..

*Vermiremediation*is the process of using earthworms to remove contaminants from soils or to decompose unrecycled compounds [27]. Several studies have reported accelerated removal of pesticides by adding earthworms to contaminated soil, but there are other studies that have shown the opposite[28]. The ability of earthworms to alter the structure, biomass, and functioning of microbial communities in soil can indirectly stimulate biodegradation of POPs, which mainly depends on microbial activity[29]. It is well known that the activity of earthworm increases the availability of nutrients (concentrations of water-soluble C and carbohydrates, as well as extracted minerals N and P), which can be used by soil microorganisms as co-metabolites, which leads to an increase in the rate of biodegradation of pesticides [30].

***Phytoremediation*.**Phytoremediation, as a new innovative technology for the restoration of POP-contaminated soils, is beginning to develop rapidly. The difficulty in the widespread adoption of phytotechnology lies in the phytotoxicity of certain pesticides (herbicides). Rhizospheric and endophytic bacteria play the main role in the degradation of POPs of pesticides. The main mechanisms of remediation of soils contaminated with organic xenobiotics are phytoextraction and phytostabilization [31-35]. The market success of phytoremediation is primarily due to the low cost of this technology. One of the reasons for cheapness is that phytoremediation technology does not require expensive equipment and specialized personnel, its methods are simple to use and the technology is suitable for cleaning a wide variety of environmental pollutants, including POPs pesticides.

Phytoremediation (from the Greek *"phyto"* - plant, and from Latin *"remedium"* - clean, restore) is a set of technologies that use different types of plants to localize, decompose, immobilize and extract specific chemical compounds from the soil.

The advantage of phytoremediation over other physicochemical methods of soil cleaning is that phytoremediation does not require special equipment, labor, additional costs and the ability to make in situ remediation. Most importantly, after phytoremediation, the soil does not lose its fertility. Therefore, this technology is environmentally friendly and economically viable [36]. In addition to the overwhelming number of advantages, phytoremediation has some limitations, such as the depth of the plant root system; the duration of the process; inappropriate climate; consumption of contaminated plants; and the use of non-local species can lead to a violation of biodiversity [31; 37]. The right choice of plant species plays an important role in the development of restoration methods (decontamination or stabilization), especially on soils with low or medium pollution [37].

Plants that accumulate toxic substances in their organs are harmful and dangerous for herbivores. The main disadvantages and obstacles to the commercialization of the technology of phyto-extraction of POPs are the length of the process and the lack of disposal technology, contaminated phytomass to reduce the transmission of pollutants through the food chain. It is believed that utilization of plant biomass is more cost-effective than direct disposal of contaminated soils. Currently, there is a way to reduce the amount of contaminated biomass using composting. Reducing phytomass will reduce the cost of transporting biomass and, accordingly, the cost of the technology. It has been established that during composting the biomass decreases to 50% [38].

***Phytoremediation of POPpesticides***

The first works on the use of phytoremediation for cleaning soils contaminated with POP pesticides were published in 1960-1970: aldrin, heptachlor and dieldrin [39]. Studies of the absorption of POPs by the plant organism root system and their translocation into the aerial part were begun in the 1970s.

These studies were generally studied from an environmental point of view to prevent the transfer of POPs through the food chain in the "plant-animal-human" system. For rehabilitation of soils polluted with POPs by plants possessing the accumulation of POPs and transferring them to the aboveground part, the last decades began to be considered. The first articles on the possibility of using plants for phytoextraction of POPs began to be published only at the beginning of 2000. After the first publications, they began to screen various plant species possessing the accumulation of POPs [32], the use of agrotechnical methods to increase the phytoextraction of POPs [33], and the mechanisms of absorption of POPs by plants. All these studies have shown that the species is *Cucurbita pepo spp. Pepo* is a promising species with phytoextraction and detoxification potential and can be used in remediation work. Scientists of the world emphasized the search for plants that possess high concentrations of POPs in shoots [34]. The authors found that the ability to absorb some compounds of POPs (DDT and their metabolites, aldrin, chlordane, dieldrin and endrin) in their shoots in high concentrations and the ability to translocate them in the "soil-root-aerial part" systemis represented by two representatives of the *Cucurbita* family - squash and pumpkin.In the articles of W. Aslund with colleagues [34] and B. Zeeb [35] there was identified that along with representatives of the genus *Cucurbita Pepo ssp. pepo* species *Carex normalis* (sedge) and *Festuca arundinaceae* (fescue) also have the ability to accumulate PCBs in their shoots. Moreover, the coefficient of biological absorption of PCBs in *Carex normalis* shoots was lower than unity and varied from 0.29-0.45 [35]. In 2013, S.K Agvebewith colleagues analyzed the concentration of organochlorine pesticides in the roots of *Cryptolepis sanguinolenta*. The analysis was carried out on 14 organochlorine pesticides: β-HCH, δ-HCH, γ-HCH, heptachlor, aldrin, γ-chlordane, α-endosulfan, p,p'-DDE, dieldrin, endrin, β-endosulfan, p,p'-DDD, p,p'-DDT and methoxychlor. The concentrations in the root samples taken during the dry season and the rainy season were compared. The average concentration of the studied POPs ranged from 0.006 mg kg-1 to 0.061 mg kg-1 in the dry season and from 0.001 mg kg-1 to 0.011 mg kg-1 in the rainy season. The total concentration of POPs also ranged from 0.033 mg kg-1 to 0.354 mg kg-1. It has been found that the uptake of organochlorine pollutants by the plant increases during the dry season [40].

From an economic point of view, despite the long recovery period of soils contaminated by POPs, phytoextraction technology is a promising technology. Future research should focus on optimizing conditions of phytoextraction from soils contaminated by POPs using plants and developing methods for the disposal of contaminated phytomass.

***Optimization of phytoremediation of soils contaminated with POP pesticides***

The effectiveness of phytoremediation depends on the degree of soil pollution, the presence and accessibility of pollutants for rhizospheremicroorganisms, absorption by roots (bioavailability), the ability of a plant and associated microorganisms to intercept, absorb, accumulate and/or destroy pollutants[41]. To increase bioavailability and increase the mobility of sorbed pollutants in soil and water systems, various chemicals areused, such as organic acids, surfactants, nanoparticles, rhamnolipids, biochar,plant-microbial associations. etc. [42-45].

*Low molecular weight compounds***.**Plant roots are known to secrete a wide range of compounds, such as organic acids (succinic, aconitic, tartaric, malic, malonic, oxalic, citric acids), sugars, amino acids and enzymes that are in complex interactions between the two abiotic and biotic components of the rhizosphere. They are distinguished by plant roots in three cases: lack of nutrients, pollutant toxicity, and anoxia [46, 47].

Organic acids are weak acids that exhibit different acidic behavior, and as organic acids dissociates into carboxylic groups, they can carry one or more negative charges, they also play an important role not only in the metabolism of energy production as intermediates in the tricarboxylic cycle but also in most cellular metabolic pathways [48]. For the first time, A.Hülster and H.Marschner [49], and later B.Campanella and R.Paul [50] hypothesized that root excretions contain substances that bind to POP molecules in the soil, forming a hydrophilic complex that can be absorbed by the root, and transported into "root – aboveground'system.B. Campanella and R. Paul [50] found that the *Cucurbita pepo* species exudates the exudates of protein origin, which bind directly to dioxins and furan molecules, thereby enhancing their hydrophilicity and facilitating translocation of their transpiration current to the aboveground part. J.C. White and colleagues [51]observed the effect of the low molecular weight organic acids and the chelating agent EDTAmixture in the different concentration (0.001–0.10 M) on the adsorption of p,p'-DDE by *Cucurbita pepo.* Established thatall organic acids significantly increased the desorption of pollutants by 19-80%: succinic acid – 19%; tartaric acid – 27%; malic acid – 31%; malonic acid – 36%; oxalic acid – 45%; citric acid – 58%; EDTA – 80%.A year earlier, J.C. White and B.D. Kottler [52]published a study on the ability of citrate to enhance absorption by plants (*Trifolium incarnatum, Brassica juncea,Vicia villosa* and *Lolium multiflorum*) p,p'-DDE from the soil. For each culture, a significant decrease in the concentration of p,p'-DDE was observed in the fractions of the soil (near the root and rhizosphere), closely associated with the plant compared to the main soil. The roots of each culture accumulated 2-5 times more pollutants than those present in bulk soil. Citrate (0.05 M) increased the concentration of p,p'-DDE in the roots *Trifolium incarnatum,Brassica juncea,Vicia villosa*by 39% compared with the vegetation that received water. In studies, the desorption of p,p'-DDE was significantly greater in the presence of 0.05 M citrate than water.

These publications indicate that phytoremediation is a controlled process; the addition of low molecular weight organic acids causes a partial dissolution of the soil structure due to the chelation of inorganic structural ions, potentially increasing bioavailability and affecting POP phytoremediation in the soil.

*Surface-active compounds.*Surfactants are chemical compounds that, when concentrated on the interface of thermodynamic phases, cause a decrease in surface tension. Surfactants can increase the possible water solubility of hydrophobic organic compounds, suggesting by encapsulating hydrophobic molecules inside the hydrophobic micelle core [53]. For example, surfactants have increased the solubility of PCBs in the soil-water system [54]. The addition of surfactants as corrections to organic polluted media was mainly used to increase the bioavailability of hydrophobic compounds by enhancing mass transfer from solid soil to the aqueous liquid phase [55].

To optimize phytoremediation conditions there are used surfactants of chemical or synthetic (Tweens, Polysorbate, Surfax, Triton, etc.) and biological origin (rhamnolipids).

M. Gonzalez with colleagues[56]found that the non-ionic surfactant Tween 80 effectively enhances the desorption of p,p-DDT, p,p-DDE and α-cypermethrin. In addition, the anionic surfactant Sodium dodecyl sulfate (SDS) enhances the desorption of p,p-DDT, p,p-DDE, α-cypermethrin, α-endosulfan and endosulfan sulfate.Synthetic surfactants have been tested in desorption experiments on soils contaminated with organic pollutants. M.T.Alcantra with colleagues[57]studied the desorption of polyaromantic hydrocarbons from the soil, testing the potential of five non-ionic surfactants (Brij 35, Tergitol NP10, Tween 20, Tween 80 and Tyloxapol) to increase the solubility of benzanthracene, fluorantene and pyrene as separate and mixed pollutants. Tween 80 removed more than 80% of the three PAHs tested as separate pollutants.

When using rhamnolipids, it was found that they as biologically active substances might be more suitable, since they are usually non-toxic and quickly decompose in the soil. Rhamnolipids are a class of glycolipids produced by *Pseudomonas aeruginosa*. When using rhamnolipid, it was revealed that the substance increases the bioavailability of p,p'-DDE for the hyperaccumulator *Cucurbita pepo ssp. pepo* and non-accumulator *C. pepo ssp. ovifera*. It has been observed that the surfactant significantly increases the biological absorption coefficient of roots, leaves, and fruits for both species. However, the biomass of *C. pepo ssp. ovifera* was reduced to 60% when the contaminated soil was treated with a surfactant and, therefore, the concentration of p,p'-DDE in the vegetative organs was very low, as in control experiments. At the same time, surfactants did not affect the biomass of *Cucurbita pepo ssp. pepo*, therefore, when treating contaminated soil with rhamnolipid, the concentration of pesticide in the vegetative organs of the plant body increased significantly. Opposite data were obtained by A.I. Lunney [58]. He noted that the addition of surfactants to high levels of contaminated soil increases the absorption of DDT by the plant. The author believes that surfactants increase the rate of POP absorption by plants; in the future, it is necessary to determine the optimal dose for various POPs for phytoremediation.

*Carbon materials***.**In recent years, more and more attention has been paid to the use of carbon-rich materials such as charcoal, such as bio-coal and activated carbon (AC), to stabilize *in situ* organic pollutants in sediments and soils [59-61]. It was revealed that the addition of activated carbon and biochar to the soil immobilizes organic pollutants, thereby reducing their bioavailability for plants, invertebrates and fish.Biochar is a charcoal-like material; a charred solid product obtained by pyrolysis in a low oxygen environment [62] and plant residues [63] and animal waste [64], while activated carbon is more a processed form of charcoal that has higher associated costs. Both biochar and activated carbon have high sorption ability due to their chemical structure, high porosity, and large surface area. While AC studies focused on soil and sediment reclamation, it was believed that this product has the strongest sorption potential [61], biochar researches have focused on improving soil quality and carbon sequestration potential. Biochar offers additional agronomic and environmental benefits, such as increased cationic soil exchange capacity, water retention capacity [65] and reduced fertilizer requirements, resulting in higher yields at lower costs. In addition, the carbon component of the biochar is stable and, therefore, can bind carbon in the atmosphere and climate change mitigation functions. A biochar is rapidly gaining popularity, but only a limited number of studies have been published on the use of a biochar to minimize the bioavailability of pollutants [66, 67], and most of these studies are based on laboratory studies. Similarly, there are studies in which AC is applied to soils in a greenhouse, as well as in the field [61] for sorption of pollutants. However, very few studies compare *in situ* biochar efficacy with AC [68], and most of them use laboratory methods of sorption [69].

It has been shown that biochar reduces the bioavailability of organic and inorganic pollutants [69, 70], as well as inorganic and organic pollutants simultaneously when added to contaminated soil [71]. In a study published in 2012, Y.Chai with colleagues[72] conducted a comparative study of the effects of activated carbon and biochar on the bioavailability of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. There was found that bioavailability increases when biochar is added, and the largest percentage in the sample with regenerated activated carbon is up to 90.7%.O.Denis [73]used activated carbon and biochar on PCB-contaminated soils to minimize the bioavailability of an organic pollutant by a plant. The concentration of PCBs in the tissues of the root of *Cucurbita pepo* was reduced by 74%, 72% and 64%, with the addition of 2.8% activated carbon, Bert's biochar and BlueLeaf biochar, respectively.

Therefore, biochar has an obvious effect on the fate and effects of pesticides and, as has been shown, affects the degradation and theirbioavailability for living organisms [74]. Despite more and more documented studies in recent years regarding the positive effect of biochar on the adsorption of pesticides than on the organic matter of the soil, the effect of biochar on the mechanisms of adsorption and desorption behavior of pesticides as effective agents affecting the bioavailability and toxicological effects of pesticides is given little attention [75-77].

*Plant-microbe associations.*Organic pollutants inhibit the development of plants, thereby reducing the effectiveness of phytoremediation [78]. To overcome development restrictions there are used the plant-microbe partnerships [79].In recent years, there are often works using microorganisms to increase the efficiency of phytoremediation and stimulate the development of a plant organism: endophytic bacteria and rhizobacteria [79]. Rhizobacteria colonize the proximity of the roots, while endophytic bacteria colonize the inside of the plant without causing pathogenicity to the host plant. Endophytic populations, as well as rhizosphere populations, are susceptible to biotic and abiotic factors, but they can be protected from them. Another advantage of endophytes is that degrading bacteria of organic pollutants are more common among endophytic populations. Endophytic bacteria with pathways of degradation of pollutants and metabolic activity can reduce both phytotoxicity and the total evaporation of volatile organic compounds [80]. Since endophytic bacteria colonize the inside of the plant, they can interact more closely with the host plant compared to rhizobacteria. Before entering the plant, endophytes must settle in the rhizosphere and attach to the root surface. Organic compounds, i.e. root exudates, act as signals for the chemotactic movement of bacteria. During the transition from the host rhizosphere to the plant endosphere, colonizing bacteria must be able to quickly adapt to a very different environment (i.e. pH, osmotic pressure, carbon source, oxygen availability). They also need to overcome the protective response of plants to invasion, that is, the production of ROS, which causes stress in invasive bacteria. The most important advantage of using endophytic degradants together with plants during phytoremediation is that any toxic xenobiotic absorbed by the plant can decompose inside the plant, thereby reducing the phytotoxic effect and eliminating any toxic effects on the herbivorous fauna living in or near contaminated sites [81].Endophytic bacteria were first used to clean soil contaminated with organochloride herbicide 2.4-dichlorophenoxyacetic acid.. Endophytic bacteria reduce the accumulation of organic compounds in plant tissues, as well as transpiration [82]. Improved degradation of pollutants correlated with an increase in the number of bacteria that decompose pollutants in plants. Some woody plants, such as poplar and willow, have been used to clean soil contaminated with various organic chemicals.Inoculation of these plants with endophytic bacteria enhanced plant growth and degradation of various organic compounds [83].

*Nanoparticles*. Nano-remediation is a new area in environmental biotechnology, which implies the ability of Ag, Au, Mg and Fe nanoparticles to cause dehalogenation of halocarbon pesticides. Nanomaterials can either directly react with a pollutant or support the conversion of a pollutant into less toxic forms [84]. Nanoparticles are used worldwide for almost 100% DDT degradation in a very short period of time [85]. Dechlorination of DDT in the aqueous phase containing the biosurfactant was performed by Gautam and Suresh [86] using the Mg/Pd bimetallic system. A high concentration of 100 ppm was successfully decomposed in a very short time, just 1 hour. It was found that bimetallic Ni/Fe nanoparticles are also effective in the degradation of DDT in an aqueous solution under weakly acidic or alkaline conditions. An acidic environment promotes efficient decomposition of DDT, since the proton production helps to generate hydrogen. Y.S. El-Temsah et al. [87]used nanosized Fe with zero valency for the efficient decomposition of DDT in water and soil. A higher decomposition of DDT (92%) was observed in water than in soil (22.4%) due to soil aging and, consequently, low diffusion rates of DDT.

Zero-valence Fe nanoparticles can completely and quickly decompose lindane within 24 hours to form γ-3.4.5.6-tetrachlorocyclohexane (an unstable intermediate), which ultimately turns into smaller benzene and chloride ions [88]. Lindane was effectively decomposed (100%) in visible light when $TiO_2$ was doped with nitrogen in a ratio of 16:1 M, while only UV radiation was observed only 37.5% decomposition [89]. Sulfide iron nanoparticles stabilized by biopolymers successfully decomposed lindane with an efficiency of 94% for 8 hours [90]. In 2016, H.P.S.Pillai and J.Kottekottil[91]investigated for the first time applied combined technology, nano- and phytoremediation, to clean soil contaminated with insecticides by endosulfan from the class of organochlorine compounds. Three types of plants, Chittaratha *(Alpinia calcarata)*, Tulsi *(Ocimum sanctum)*, and Lemongrass *(Cymbopogon citratus)*, absorbing endosulfan from the soil in the absence and presence of zero-valence iron nanoparticles (nZVIs) (1000 mg/kg of soil) were used in the experiment. The initial concentration of endosulfan in the soil is 1139.84 ± 0.93 µg/kg. In the experiment, there were the following options: control; control with the addition of zero-valence iron nanoparticles; *Alpinia calcarata* (phytoremediation); *Alpinia calcarata* (nano-phytoremediation); *Ocimum sanctum* (phytoremediation); *Ocimum sanctum* (nano-phytoremediation); *Cymbopogon citratus* (phytoremediation); *Cymbopogon citratus* (nano-phytoremediation). Soil measurements were carried out on the $7^{th}$, $14^{th}$, $21^{st}$ and $28^{th}$ days. *A. calcarata* had better efficacy compared to two other plant species, and the efficiency decreased in the following order: *A. calcarata* >*C. citratus*>*O.sanctum*. The initial rate of endosulfan removal was high (82% was removed within 7 days) when nanophytoremediation experiments with *A. calcarata* were performed, but then gradually decreased, probably due to the fact that nZVI activity decreased over time.Thus, the combined technology of nano- and phytoremediation is one of the promising areas for the remediation of organochlorine pesticides.

**Conclusion**

One of the key areas of the Strategic Plan until 2020 is the green economy and the environment. However, the problems associated with the state of the environment remain unresolved: land degradation, high levels of air and soil pollution. The development and implementation of green technologies remains a priority in environmental biotechnology. In this regard, as part of a doctoral dissertation, the Institute optimizes the technology of phytoremediation of soils contaminated with POPs pesticides using Tween 20 and biochar. The bioenergetic species *Miscanthus sinensis* and *Paulownia tomentosa* are used as an object of study. They are considered as a promising industrially significant cellulose-containing raw material for the production of cellulose, biofuels and chemicals because of their high productivity in order to save forest wealth, and at the same time, they have phytoremediation potential.

*Paulownia tomentosa* is receiving increasing attention due to its market value for the production of wood and biofuels, due to its rapid growth, high biomass production (150 t/ha per year) and increased resistance to stress.

*M. sinensis* is a highly productive, frost-resistant species and have ability to restore the contaminated soil by POPs. Nowadays, itis actively considered as a new source of cellulose.

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## ТОЛ ПЕСТИЦИДТЕР ЖӘНЕ РЕКУЛЬТИВАЦИЯ ӘДІСТЕРІ (ШОЛУ)

**Аннотация.** Қазақстан Республикасының стратегиялық даму жоспарының маңызды бағыттарының бірі ТОЛ-пестицидтерімен ластанған ошақтарын мұқият талдау және ластанған топырақтарды қалпына келтіру әдістерін жасау болып табылады. ТОЛ пестицидтерінің өндірісінің көптішілігі, оларды агроөнеркәсіптік компанияларымен артық сатып алынуы, сонымен қатар колхоздар мен совхоздардың таратылуы және жерді жекешелендіруімен байланысты ауылшаруашылық инфрақұрылымдағы өзгерістер көптеген ТМД елдерінде, соның ішінде республикамыздың қоймаларында олардың жиналуына әкеліп соқты. Олар қоршаған ортаға жаңбырмен, желмен, сутасқыны, көшкін және өрт салдары кезінде, жергілікті және бүкіл әлем деңгейінде адам денсаулығына және қоршаған ортаға экологиялық қауіпті өндіреді.

Осыған байланысты мақалада ТОЛ-пестицидтерімен күресу мәселелері және топырақтың құнарлылығын қалпына келтіру әдістері туралы әдеби шолу ұсынылған. Ескі пестицидтерді жоюдың заманауи әдістері (оқшаулау, көму, иммобилизация, топырақты жуу, электро-рекльтивация, термиялық өңдеу және т.б.) және пестицидтермен ластанған топырақтың құнарлылығын қалпына келтіруәдістері (биоремедитация, фиторемедитация, вермиредитация) қарастырылған. Топырақтағы ТОЛ пестицидтерін фиторедитациялау технологияларына және олардың тиімділігін арттыру әдістеріне ерекше назар аударылды, өйткені бұл технология экономикалық тұрғыдан тиімді және экологиялық таза технология. Өсімдік ағзасының дамуын ынталандыру, ТОЛ пестицидтерінің фитоқолжетімділігін және топырақпен су жүйелерінде қозғалғыштығын арттыру үшін химиялық заттармен (төмен молекулалық қосылыстар, көміртекті материалдар (биочар) және наноматериалдар) өсімдік-микробтық бірлестіктерді қолдана отырып, қоршаған ортаны оңтайландыру шарттары жан-жақты қарастырылды.

**Түйін сөздер:**ТОЛ-пестицидтер, рекультивациялау, фиторемедиация, оңтайландыру, қоршағанорта

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## СОЗ-ПЕСТИЦИДЫ И СПОСОБЫ РЕКУЛЬТИВАЦИИ (ОБЗОР)

**Аннотация**. Тщательный анализ очагов загрязнения СОЗ-пестицидами и разработка методов рекультивации загрязненных территорий является одним из ключевых направлений стратегического плана развития Республики Казахстан. Огромное производство СОЗ-пестицидов, чрезмерная закупка их агропромышленными компаниями, а также изменения инфраструктуры сельского хозяйства, связанные с ликвидацией колхозов, совхозов и приватизацией земель привело к их накоплению в складах во многих стран СНГ, в том числе Республике. Они, попадая в окружающую среду с дождем, ветром, в результате наводнений, оползней и пожаров представляют экологическую опасность для здоровья человека и окружающей среды, как на местном, так и на глобальном уровне. В связи с этим, в статье представлен литературный обзор о проблемах СОЗ-пестицидов и способах их рекультивации. Рассмотрены современные способы утилизации устаревших пестицидов (изоляция, захоронение, иммобилизация, промывка почвы, электро-рекультивация, термическая обработка и др.) и методы рекультивации пестицид-загрязненных земель (биоремедиация, фиторемедиация, вермиремедиация). Особый акцент в статье уделили технологии фиторемедиации СОЗ-пестицидов в почве и методам повышения их эффективности, так как данная технология является экономически выгодной и экологически безопасной технологией. Подробно рассмотрены условия оптимизации среды, с помощью химических веществ (низкомолекулярные соединения, углеродные материалы (биочары) и наноматериалы) и растительно-микробных ассоциации для стимуляции развития растительного организма, повышения фитодоступности СОЗ-пестицидов и увеличения их подвижности в почвенных и водных системах.

**Ключевые слова:** СОЗ-пестициды, рекультивация, фиторемедиация, оптимизация, окружающая среда

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