Chapter 8
Sustainable Strategies of Phytoremediation of the Sites Polluted with Obsolete Pesticides

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Abstract The land around former warehouses has an increased likelihood of contaminant exposure for local population. For phytoremediation of phytotoxic soil, polluted with pesticides, around the former warehouses, we propose a method of phytoremediation using phytotoxicity tolerant plants. In a soil polluted with wide range of obsolete pesticides, changes in quantitative proportions of plant species, structure, productivity and floristic features are observed. In the structure of such phytocenosis, perennial plant species with vegetative reproduction prevail. Current study demonstrates that pesticide-tolerant wild plants decrease DDT concentration in soil by rhyzodegradation and rhyzostabilization of the pesticide. Wild plants with translocation factor, i.e. the ratio of concentration in the shoots over the root concentration, below 1 are suitable for phytostabilization of DDT and prevention of its migration in conditions of polycomponent pesticide pollution. Resistance to a high pesticide pollution of pesticide-tolerant plants is acquired during vegetation under the influence of persistent toxicants.

Keywords Dichlorodiphenyltrichloroethane (DDT) • Phytoremediation • Phytostabilization • Rhyzodegradation • Persistent organic pollutants (POPs)

8.1 Introduction

Management of semi-natural ecosystems, which have been exposed to different complex pollution, as well as remediation of former industrial sites contaminated with radionuclides, heavy metals or organic compounds, is of major concern in

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K. Vitale (ed.), *Environmental and Food Safety and Security for South-East Europe and Ukraine*, NATO Science for Peace and Security Series C: Environmental Security,
DOI 10.1007/978-94-007-2953-7_8,

several European countries. For example, uranium mining and milling, phosphate processing or coal mining resulted in high accumulation of radionuclides and/or heavy metals in the soil surface layers of the surrounding environment. Contamination also could be caused by accidents at nuclear power plants, similar to the Cherobyl incident occurred in 1986.

Soil pollution is a serious environmental problem, not only in the highly industrialized western countries, but also in developing countries. Polluted areas are very dangerous for people and ecosystems. The extent of pollution and its characteristics vary widely. A substantial portion of polluted sites consists of large areas where the surface soil is more or less diffusely polluted with pesticides. These pesticides are often persistent organic pollutants (POPs), and their decomposition in nature is very slow.

Many republics of the former Soviet Union, including Ukraine [1], accumulated large reserves of persistent pesticides during the existence of the Soviet Union. Many of these reserves are now stored in bad conditions and serve as a source of POPs pollution of surrounding agricultural lands. There are substantial health threats to the population from poisoning of surface water from pesticide residues suspended in the air, and from groundwater pollution as a result of the vertical migration of pesticides [4].

Accordingly to the Ministry of Ecology and Natural Resources of Ukraine, at the end of 2009, the amount of obsolete pesticides and agricultural chemicals in Ukraine was about 21 t. The total number of warehouses is about 3,000. In addition, there are about 2,000 contaminated areas located on sites of destroyed warehouses.

Some of these warehouses are located in the areas affected by the Chernobyl accident. As known from scientific sources, the combined action of pesticides and radionuclides may have a synergistic negative impact on wildlife and human population. In 2010, the Ministry of Ecology and Natural Resources began implementation of a major program of cleaning of hazardous wastes in Ukraine. In particular, the Ministry planned to solve the problem of obsolete pesticides completely by the end of 2012. This is one of the priority programs of the Ministry. Given the lack of the pesticide destruction capacities in Ukraine, pesticides will be transported for safe disposal to specialized factories outside Ukraine.

Nevertheless, the problem of remediation of soil polluted with POPs remains unsolved. Two aspects of obsolete pesticides problem could be indicated. Firstly, there are obsolete pesticides that are stored in warehouses; secondly, there are pesticides in the soil. Polluted soil cannot be cleaned using known physical or chemical methods due to extremely high cost of transportation and processing of large soil quantities [3].

Our team examined soil samples taken from areas around pesticide warehouses in Kiev, Khmelnitsky, Vinnitsa, Zhitomir and Chernovtsy regions of Ukraine. Analysis of these samples conducted in the Institute of Agroecology revealed concentration of DDT and its metabolytes of 100–10,000 μg/kg and concentration of sim-triazine herbicides about 500 μg/kg. Pesticide residuals had been found at the distance of 500 m from the warehouse and at the depth of 6 m [16, 17]. Those studies confirmed the actuality of the problem of pesticide warehouses as sources of environmental POPs pollution. An important aim of research in the field of neutralization of pesticide polluted objects is development of long-term strategy of soil and water phytoremediation.

8.2 Phytoremediation of Polluted Soil

Phytoremediation is a complex of "green" technology that uses plants for remediation of soil, sediments, and surface and ground water polluted with toxic metals, organic pollutants and radionuclides. Phytotechnologies do not require large investments. They are effective and inexpensive tools of soil remediation [18, 24]. Phytotechnologies are more profitable than any alternative mechanical or chemical method of soil pollution treatment. They are also ecologically safe. It was concluded that plants have genetic potential to remove or block a wide range of pollutants [14]. A large-scale research was conducted on phytoextraction of inorganic elements [13] revealing a number of plant species capable to hyperaccumulate metals [25]. Mechanisms of accumulation of chemical elements by plants were also investigated [2].

Phytoremediation of organic pollutants originally was developed for three classes of compounds: chlorine solvents, explosive materials and petroleum hydrocarbons. Recently, phytoremediation was also studied for soil remediation from POPs and polycyclic aromatic hydrocarbons (PAHs). POPs include industrial chemicals, byproducts of chlororganic synthesis and some chlorine-containing pesticides: DDT, hexachlorocyclohexane (HCH), chlordane, aldrin, dieldrin, and mirex. All these compounds have a long half-life in the environment and are able to bioaccumulate in trophic chains. They exert many negative effects on human and animal organisms, such as immunodepressive, cancer-causing, mutagenic, and teratogenic effects [15]. DDT and HCH were widely used in Ukraine in the past as insecticides for plant protection.

The goal of phytoextraction is to accumulate as much pollutants as possible in the vegetative part of the plant to clean the soil. In order for a plant to be classified as a hyperaccumulator of pollutants, the plant has to produce a large biomass, and the concentration in the ground part of the plant has to be considerably higher than concentration in the underground part [13]. The translocation factor represents the ratio of pesticide concentration in the shoots over the root concentration. If the translocation factor is greater than unit, processing of polluted plants is more efficient than processing of polluted soil [23].

Earlier studies and our research revealed great perspective in the use of phytotechnologies for remediation of soil polluted with POPs [22, 19]. However, soil polluted with a wide range of pesticides is often toxic for known remediator plants. Phytotoxicity of soil is an obstacle for use of phytotechnologies. For example, cultural plants, that are able to accumulate POPs, are dying after 30–35 days of vegetation. Plants intended for use in phytoremediation of soil contaminated with organochlorine insecticides and persistent herbicides should be tolerant to these pesticides. Thus, there is an urgent need to find remediator plants, which are tolerant to soil phytotoxicity, and study their phytoremediation capabilities.

8.3 Materials and Methods

To characterize the residual amount of pesticides in soil near the pesticide warehouses, we studied organochlorine pesticide 4,4′-DDT and its metabolites (4,4′-DDE, 4,4′-DDD). Soil and plant sampling was conducted according to engineering specifications and state standards for Ukraine [7, 11]. Rhizosphere soil sampling was conducted according to methods of soil microbiology [26]. At each location, plant species' identity and coverage were determined within four 50 × 50 cm squares using Roshensky grids [5]. Common plant species were selected to estimate plant uptake of DDT metabolites. The sampled plants were carefully cleaned and separated into roots and shoots for analysis.

Organochlorine pesticides were quantified by gas chromatography (GC) using electronic-capture detector (ECD) according to accepted engineering specifications and state standards of Ukraine [8, 10, 12]. Vegetative studies were conducted in climatic chambers [6, 9]. Soil phytotoxicity was studied according to international and Ukrainian standards ISO 11269(1–2).

8.4 Plant Selection

The purpose of this study was to find plant species persistent to pesticides and capable either to accumulate large concentrations of pollutants or decompose organic xenobiotics in the rhizosphere.

During the process of natural plants settlement on the territories polluted with xenobiotics, changes in physical, chemical and biological properties of soil are observed. With development of secondary succession, persistent plant groups that include tolerant plant species are formed. Those tolerant species show potential for use in phytoremediation of such soil.

Our experiments were conducted to observe the adaptation processes of wild plants on a soil highly polluted with pesticides. The experiments were conducted in the climatic chamber. Gray sandy podzolized soil polluted with organochlorine pesticides and persistent herbicides was sampled near the pesticide warehouse in Kyiv region from the depth of 0–30 cm. The following plants of local phytocenosis were selected for the experiments: *Taraxacum officinalis* Wigg., *Oenothera biennis* L., *Erigeron canadensis*, *Xanthium strumarium* L., *Potentilla argentea* L., *Daucus carota* L., *Plantago lagopus* L., *Achillea millefolium* L. Each plant was vegetated separately in 51 plastic pots with 3 pots per species. The seeds of these plants were picked on unpolluted territory.

The observations of the adaptation processes of *Taraxacum officinalis* Wigg., *Oenothera biennis* L., *Potentilla argentea* L., and *Daucus carota* L. were conducted during 2 years (2 vegetation periods). Plants *Xanthium strumarium* L., *Plantago lagopus* L., *Erigeron canadensis* L. and *Achillea millefolium* L. were vegetated for one vegetation period.

For the plants growing on polycomponent polluted soil from seeds, visible toxicity symptoms were found for the following plant species: *Taraxacum officinalis* Wigg., *Plantago lagopus* L.i *Oenothera biennis* L. – point necrosis, yellowing and dying off of lover leaves; for *Potentilla argentea* L. and *Achillea millefolium* L. – decrease of growth processes and miniaturization of habitus; for *Xanthium strumarium* L. – dying off of leaves borders. Visible morphological changes were not observed on *Daucus carota* L. and *Erigeron canadensis* L.

The change of leave color, necrosis marks, chlorosis, yellowing and dying off of the lower leaves are non-specific reaction of plants to toxic influence of pesticides in soil. Such damages are classified as chematotraumosis [20]. Premature yellowing of leaves is followed by a major breach of metabolism. In chlorotic leaves, concentrations of the non-protein forms of nitrogen and ash elements increased, and their proportions changed. In addition, the amount of dry matter decreases, concentration of water increased, many ferments became less active, and osmotic pressure and suction force increased. Total concentration of organic acids in such leaves is always high [20]. In addition to mentioned symptoms of toxicity, the decrease of growth rate of all studied plants was detected. This phenomenon is caused by oppression of synthetic functions of plants, which are critical for the growth processes [20].

Weakened synthesis of organic compounds as the result of reduction of the leave area decreases reproductive ability of the studied plants. During the first year of study, only *Xanthium strumarium* L. had fruit (with recessed size). *Daucus carota* L. in its second year and *Erigeron canadensis* L. have formed seeds at the end of vegetation. *Taraxacum officinalis* Wigg., *Oenothera biennis* L. and *Potentilla argentea* L. did not form flowers and fruits even after 2 years of vegetation.

These studies showed difference in the reaction of plants on polycomponent pesticide pollution of soil, while growing from seeds, and in the field under the chronic influence of the pollution, where above phenomena did not take place. This difference can be explained by few reasons. Firstly, the compensation of the negative pesticide influence is much more effective on the group level in the field than on the species level in pots [20]. Secondly, the species with wide geographical distribution almost always form populations adapted to local conditions by physiological adaptation or producing new genetic types (with morphological differences or without them). Herewith, the cell adaptation is the most important feature of plants exposed to a long-term adverse toxicant influence [21]. There are biotypes of plants species formed in the field, which are persistent to local soil toxicants. These plants have seeds carrying genetic information for adaptation to local conditions, including pollutants.

The resistance of plants to pesticides in the field is revealed only when the population of persistent plants reaches at least 30% of total population.

Table 8.1 Distribution of DDT between root and shoot tissue for the pesticide-tolerant plants grown on contaminate soil (vegetative experiment)

Name	Soil or tissue	Total DDT, μg/kg dry matter	Translocation factor
Xanthium strumarium L.	Soil	398.0 ± 2.5	0.40
	Root	304.1 ± 11.1	
	Shoot	118.4 ± 3.3	
Achillea millefolium L.	Soil	757.9 ± 0.7	0.15
	Root	1,090.4 ± 18.3	
	Shoot	163.9 ± 3.9	
Achillea millefolium L.	Soil	1,567.0 ± 1.9	0.27
	Root	1,701.3 ± 18.0	
	Shoot	466.9 ± 5.1	
Plantago lagopus L.	Soil	543.9 ± 14.7	0.21
	Root	1,727.9 ± 41.1	
	Shoot	362.8 ± 12.3	

Development of this phenomenon in agriculture is prevented using different alternating herbicides and a crop rotation [21]. Hence, under the influence of negative factors, plants are able to expand the toxicity tolerance limits by changing the orientation of synthesis processes – decomposition of physiologically active compounds in plant cells or regain of normal growth rate by adapting on the cell or genetic level.

Beside phenological observation of growth and development of plants in climatic chamber, we conducted research of phytoextractional and phytodegradational ability of wild plants. We studied the following species, present in the phytocenosis formed in conditions of long-term polycomponent pesticides pollution: *Xanthium strumarium* L., *Achillea millefolium* L., *Plantago lagopus* L.

To evaluate the washout of toxicants during watering of plants, we used soil sample, polluted with DDT and its metabolytes, without plants. Experiments included determination of HCH residuals in soil of every pot before and after the experiment, and also in vegetative organs of plants.

The study of the accumulation and degradation of DDT in *Xanthium strumarium* L., *Achillea millefolium* L., and *Plantago lagopus* L. at various levels of DDT pollution, has shown that these plants mainly accumulate toxicants in the root system with low translocation factor (Table 8.1).

For all studied wild plants, a significant decrease of toxicants concentration in soil compared to the original levels occurs (Table 8.2). Depending on the species, total DDT concentration decreased by 15.2–30.7% (4.4–19.9% in the pot soil). Hence, wild plants cause a decrease of DDT and its metabolites in soil having long-term polycomponent pesticide pollution. Notably, concentration of HCH had decreased by 3.6% due to watering.

Table 8.2 Decrease of DDT concentration in soil as the result of growing persistent to phytotixicants plant species (vegetative experiment)

Plant species	Before the experiment: Total DDT, μg/kg dry soil, in pot soil	After the experiment: Total DDT, μg/kg dry soil, in pot soil	After the experiment: Total DDT, μg/kg dry soil, in rhyzospheric soil	After the experiment: Decrease in rhyzospheric soil, %	After the experiment: Total decrease, %
Xanthium strumarium L.	398.0 ± 2.5	359.9 ± 1.0	276.0 ± 3.9	30.6	19.9
Achillea millefolium L.	757.9 ± 0.7	659.6 ± 64.6	564.7 ± 1.7	25.5	13.0
Achillea millefolium L.	1,567.0 ± 1.9	1,445.4 ± 15.8	1,328.7 ± 2.4	15.2	7.8
Plantago lagopus L.	543.9 ± 14.7	520.1 ± 50.8	445.4 ± 1.7	18.1	4.4
Soil only	1,253.3 ± 37.5	1,208.0 ± 1.9	–	–	3.6

8.5 Conclusions

The persistence of plant species *Taraxacum officinalis* Wigg., *Oenothera biennis* L., *Erigeron canadensis*, *Xanthium strumarium L.*, *Potentilla argentea L.*, *Daucus carota L.*, *Plantago lagopus L.*, *Achillea millefolium L.* tolerant to high pollution level was studied. It was shown that tolerance to the pesticide pollution is gained during the vegetation process in conditions of chronic toxicant influence.

Wild plant species *Xanthium strumarium L.*, *Achillea millefolium L.*, *Achillea millefolium L.*, *Plantago lagopus L.* have low translocation coefficients, but are able to grow on phytotoxic soil and decrease DDT concentration by phytostabilization and rhyzodegradation.

Local citizens are advised to assist in planting of wild plants on polluted sites. Fencing of these sites and monitoring of the soil and plant pollution by pesticides and their metabolites is essential.

Acknowledgement Authors express their thanks to COST ACTION 859 and COST ACTION FA 0905 for financial support.

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