PHYTOTECHNOLOGIES FOR MANAGEMENT OF RADIONUCLIDE AND OBSOLETE PESTICIDE CONTAMINATED SOIL IN UKRAINE

Lidiya Moklyachuk, Volodimir Patyka, Institute of Agroecology and Biotechnology, Kyiv, Ukraine;
Peter Kulakow, Kansas State University, USA
Boris Sorochinky, Institute of Cell Biology and Genetic Engineering, Kyiv, Ukraine

Environmental pollution of soil with radionuclides after of the Chernobyl accident and with obsolete pesticides from abandoned pesticide storage warehouses is one of the greatest ecological problems for Ukraine. Radionuclide pollution covers a large area of Ukraine, including the Chernigov, Kiev, Zhitomir, Rivne and Volyn regions.

A substantial portion of polluted sites consist of large areas where the surface soil is more or less diffusely polluted with pesticides. These pesticides are often highly stable organic pollutants and are not easily biodegraded in nature.

Introduction



Soil pollution is a problem which society faces worldwide. Among the pollutants, radionuclides and organic chemicals are of special concern due to their harmful effects. Contaminated sites may cause severe risks to humans and ecosystems. The extent and the characteristics of polluted sites vary widely.

In many Ukrainian regions, abandoned warehouses store large quantities of pesticides, including many organochlorine pesticides. Inventories have determined there are 147 storehouses under federal government control and 4,976 warehouses located on farms (Table 1). The total estimated weight of bulk pesticides is 13,574 tones.

Region	Number of warehouses	
	Under Federal Control	On Farms
Republic Crimea	2	190
Vinnitsa	7	16
Volyn	14	188
Dnipropetrovsk	5	255
Donetsk	1	355
Zhitomir	8	150
Zakarpattia	5	49
Zaporizhia	3	253
Ivano-Frankivsk	-	136
Kyiv	9	226
Kirovograd	9	264
Lugansk	-	207
L'viv	9	221
Mykolaiv	6	190
Odessa	11	145
Poltava	6	244
Rivne	-	48
Sumi	5	432
Ternopil	2	136
Kharkiv	26	358
Kherson	5	51
Khmelnitsky	2	296
Cherkasy	1	271
Chernivtsi	1	32
Chernigiv	10	263
Total	**147**	**4,976**

Table 1: The number of obsolete pesticide warehouses in the regions of Ukraine.

In our opinion, the most actual problem for all the NIS is obsolete pesticides and their storehouses. There were very large number of them on the territory of former USSR.

There are substantial human health threats from pesticide residues in surface water, in groundwater as a result of the vertical migration, and suspended in air. In the Ukrainian countryside the majority of the people drink water from wells. The depth of these wells is commonly about 20 meters. Water in the wells is frequently polluted with nitrates and persistent pesticides.

The Institute of Agroecology and Biotechnology of Ukrainian Academy of Agrarian Sciences conducts investigations of obsolete pesticides pollution of agricultural territories.

To characterize the residual amounts of pesticides in soil near pesticide warehouses we studied soil contamination with organochlorine pesticides and their metabolites (α-, β-,γ-HCH, 4,4'-DDT, 4,4'-DDE, 4,4'-DDD, 2,4'-DDT, 2,4'-DDE, 2,4'-DDD). The locations we had researched research are five pesticide storehouses and the land surrounding these facilities. They are located in different regions of Ukraine:

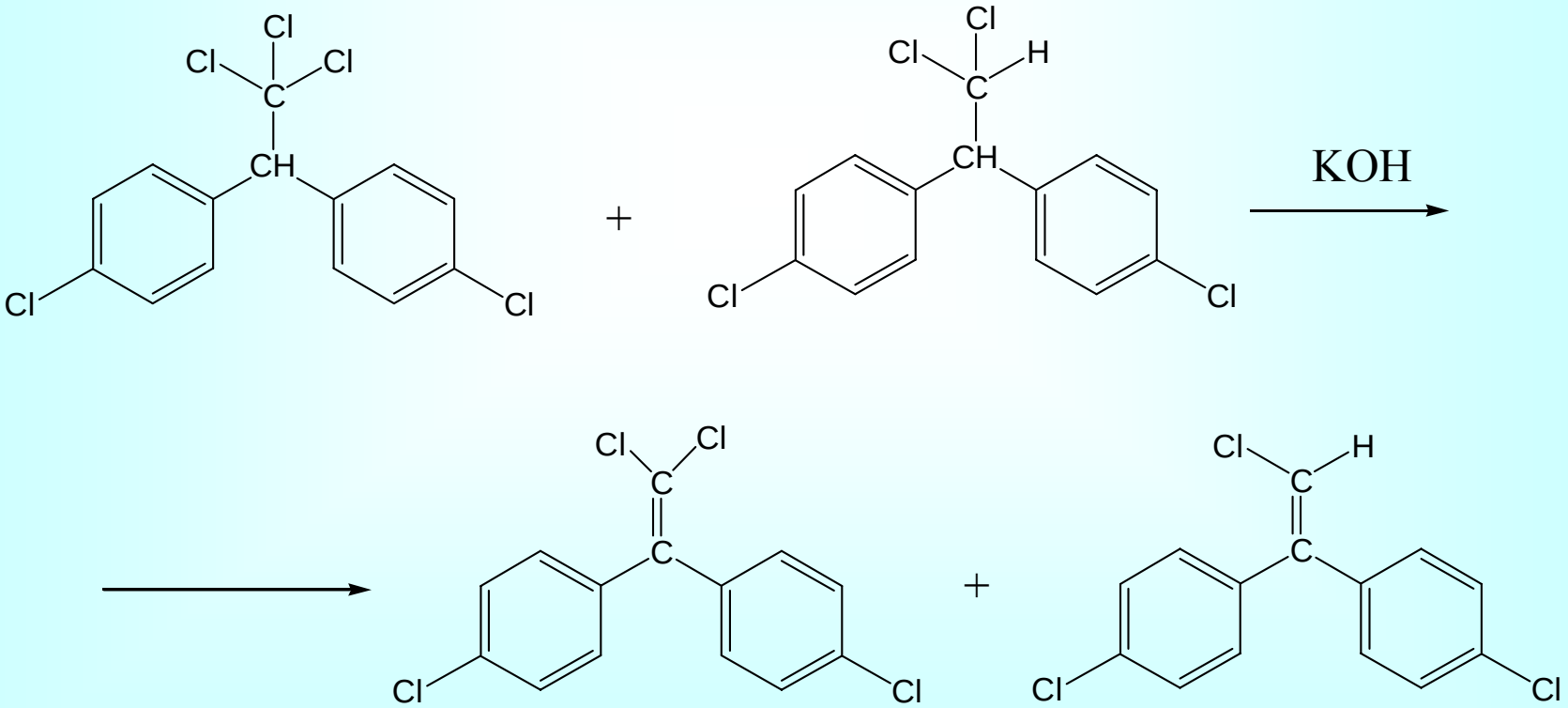
- Kyiv region - north
- Preserve Askaniya Nova – south
- Khmelnitsky region – west
- Vinnitsa region – center.

The identity and concentration of pesticides at the contaminated sites has not been established.

Sampling was conducted according to accepted engineering specifications and state standards for Ukraine. Soil samples were taken from six distances from a warehouse – 1, 5, 10, 15, 25, 50 meters in four directions – northern, southern, western and eastern, and from soil depths of 0-20, 20-40, 40-60, 60-80, and 80-100 cm of soil. All soils and plants were analyzed by the Institute of Agroecology and Biotechnology. Organochlorine pesticides were quantified by gas chromatography (GC) using an electronic-capture detector (ECD) according to accepted engineering specifications and state standards for Ukraine.

While conducting gas chromatography for quantifying organochlorine pesticides, we noticed the presence of large quantities of unidentified compounds with retention times greater than that for 4,4'-DDT.

These samples were processed with KOH solution resulting in chemical transformation of DDT to DDE.



The comparison of chromatograms of samples after treatment with KOH and chromatograms of Arochlor standards showed the presence of polychlorinated biphenyls (PCBs) in the samples. This can be explained by past treatment of orchards with PCB containing pesticides. Results are shown in Table 2

Table 2. Concentrations of organochlorine compounds in the arable layer of soil from pesticide warehouse pollution zones (units in µg/kg).

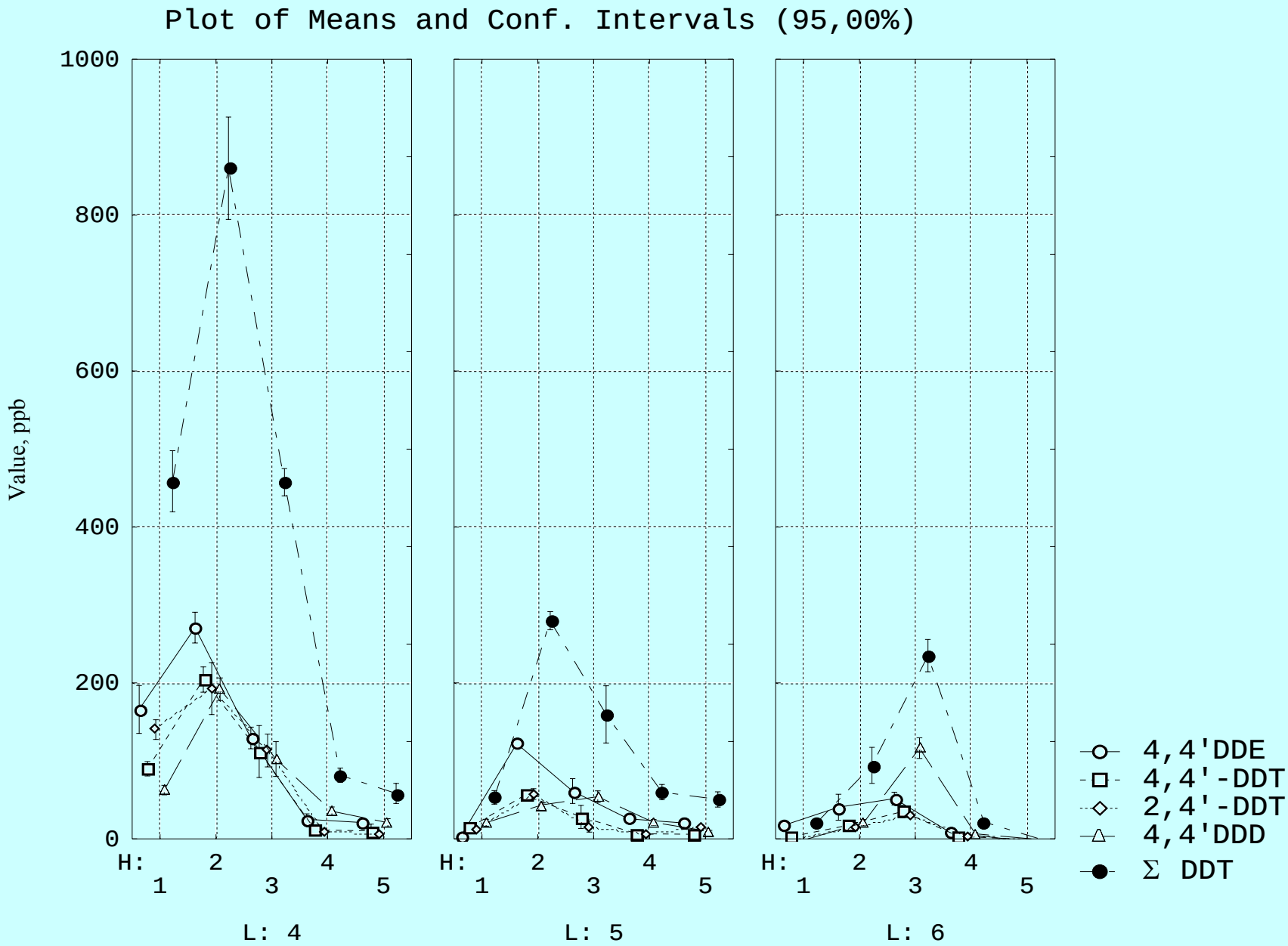
Location of storehouse	4,4'-DDE (min-max)	4,4'-DDT (min-max)	4,4'-DDD (min-max)	2,4'-DDT (min-max)	Sum of 4,4'-DDT, 4.4'-DDE, 4.4'-DDD, 2.4'-DDT, 2,4'.-DDE, 2,4'-DDD (min-max)	Sum α-, β-,γ-HCH (min-max)	PCB (max)
Kyiv region Vasilkyvskiy area	1.0-218.0	2.0-86.0	6.0-246.0	4.2-99.4	15.3-667.0	7.0-826.0	no data
Biospherical preserve Askaniya – Nova	0.5-421.4	8.2-1019.8	5.8-179.8	2.8-57.5	18.8-1696.5	15.8-616.5	692.2
Khmelnitsky region v. Samchyky	9.0-366.3	2.8-595.5	7.3-899.2	3.3-31.2	26.5-1908.5	1.5-2030.6	no data
Vinnitsa region	1.2-66.1	0.2-16.6	0.3-61.7	0.5-26.6	2.2-175.2	1.5-17.0	no data
*Kyiv region Makarivsky area	2720.1	12310.4	3961.2	3103.3	2632.5	182352.2	no data

* The samples of soil investigated are selected on 1 point on distance 5 m from a warehouse from the depth 0-20sm

Results from soil analyses at pesticide storage sites have shown that the field sites are contaminated with the metabolites of DDT and the isomers of HCH. As Table 2 shows, the maximum concentrations observed from all sites were: 4,4'-DDE – 2720.1 μg/kg, 4,4'-DDT – 12310.4 μg /kg, 4,4'-DDD – 3961.2 μg//kg, 2,4-DDT – 3103.3 μg /kg, sum. α-, β-,γ-HCH – 182352.2 μg /kg. These results are describing a great potential health danger to neighboring towns and farms.

The pollution spreads irregularly, but also there is a general trend for pollution levels to decrease with soil depth and increasing distance from a pesticide warehouse (Figure 1). Units of concentration are in μg/kg.

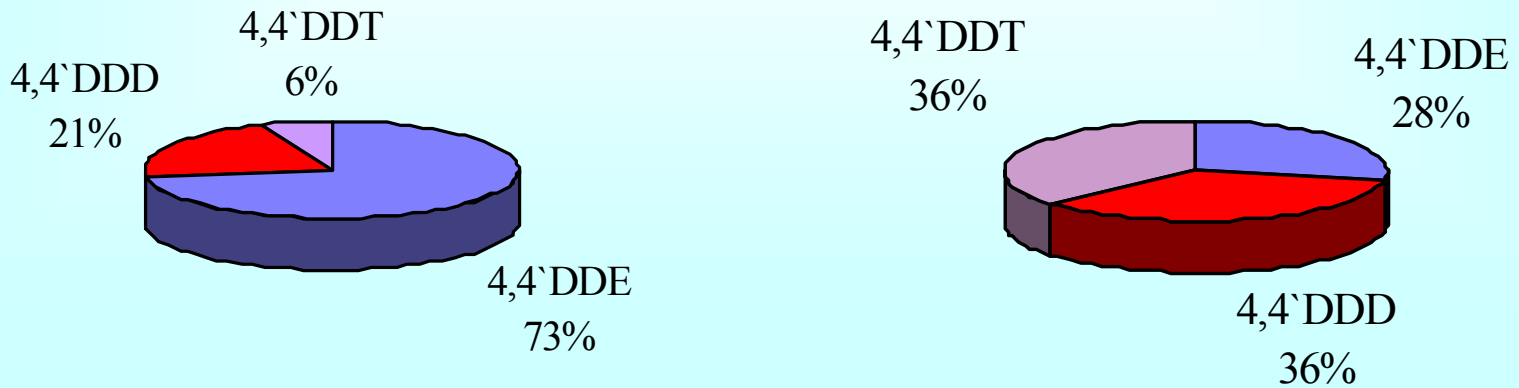
Figure. 1. Distribution of DDT residuals in soil at 5 soil depths (H1=0-20, H2=20-40, H3=40-60, H4=60-80, H5=80-100 cm) and 3 distances from the pesticide warehouse (L=10, 15, 20 m). The warehouse is located in the Khmelnitsky region, v. Samchyky.



In spite of different geographic locations and different climatic conditions such as temperature regime, we noticed a common pattern of high concentrations of residual DDT and its metabolites. Since high levels of pollution may cause soil sterilization, the microbiologist of our institute began the microbiological investigations of the polluted soils.

Arable soils were also investigated. Concentration of pesticides in the soils of arable land of given in the sample regions did not exceed acceptable values. In these soils, the concentration of residual HCH was 0-13 µg/kg and the total concentration of DDT metabolites was 0-35 µg/kg. This pattern shows that POPs containing pesticides have not been used in recent years (Figure 2)

Figure 2. Circle diagram of the relative quantity of 4,4'-DDT:4,4'-DDE:4,4'-DDD in the arable lands and in soil around pesticide warehouse (2001-2002)



Besides high concentrations of organochlorine pesticides, plots near some warehouses are polluted with persistent herbicides, such as atrazine, prometryn, dicamba, 2,4-D, and trifluraline. We conducted research on the soil content of the persistent herbicides in the soils near pesticides warehouses. The results are shown in Table 3.

Table 3: Concentration of persistent herbicides in the arable layer of soil from the area near pesticide warehouses (units in µg/kg).

Location of storehouse	Simazine	Atrazine	Prometryn	Year of the research
Vinnitsa region	5000	400	800	2004
Zhitomir region	2500	500	500	2004
Zhitomir region (Water from the river near the storehouse)	12.5	5.1	2.5	2004
Maximum acceptable concentration in river's water	2.4	5.0	3.0	

There are more than 5 thousand pesticide warehouse sites in Ukraine. Some of these still store pesticides, others are ruined, and other sites now are only represented by the presence of polluted soil. To stop the soil pollution and toxicant migration it is necessary to propose low-cost and ecologically-safe remediation methods. We think that phytoremediation is a likely suitable method for restoring these areas.

These sites are contaminated with organochlorine pesticides, including high quantities of original 4,4-DDT. We had begun to study phytoextraction abilities of vegetable marrow (*Cucurbita pepo)* when grown in typical Ukrainian soils contaminated with organochlorine pesticides. We have conducted greenhouse experiments on DDT phytoextraction.

We used a commercial preparation of DDT in a gray forest soil. The original technical grade DDT contained: 57.6% 4,4'-DDT, 31.5% 2,4'-DDT, 1.2% 4,4'-DDE, 0.5% 4,4'-DDD and 4.8% (2,4'-DDE, 2-4'-DDD and unidentified compounds). *C. pepo* was chosen from the literature as a potentially effective phytoremediator. Plants were grown until the beginning of flowering and then analyzed for pesticide uptake. We think that it may be dangerous to grow these phytoremediator plants beyond the beginning of reproduction since the flowers and fruits may contain compounds that are toxic to insects or people (Figure 3).

Figure 3. The research of phytoextraction abilities vegetable marrow (Cucurbita pepo) from typical Ukrainian soils

We obtained good results, which confirm the ability of *C. pepo* to extract DDT from a typical Ukrainian gray forest soil. As table 4 shows, the processes of phytoextraction and phytodegradation flows simultaneously in the plants.

Table 4: Content of 4,4′-DDT and 4,4′-DDE in the soil and in plant tissue of vegetable marrow, Cucurbita pepo (units in µg/kg).

	4,4′-DDT	4,4′-DDE	Ratio: 4,4′-DDE/ 4,4′-DDT
Soil	920	20	1 :46
Plants (fresh)	103	9	1 : 12

Unfortunately, the current funding of this work does not allow us to conduct research more widely and to test and introduce practices at contaminated locations. Further research has been proposed involving the Institute of Agroecology and Biotechnology of the Ukrainian Academy of Agrarian Sciences, Institute of Cell Biology and Genetic Engineering of the National Academy of Science of Ukraine and Kansas State University. The title of the proposed project is ***"PHYTOTECHNOLOGIES FOR MANAGEMENT OF RADIONUCLIDE AND PESTICIDE CONTAMINATED SOIL IN UKRAINE"***. This project has theoretical and practical value. The investigation of consortia of plant species for successful phytoremediation of pesticide contaminated soils would have application in Ukraine and other countries. Additional benefits would come from practical applications that could address sites with human health risk from mixed contamination with both pesticides and radionuclides.


THANK YOU VERY MUCH FOR YOUR ATTENTION