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## REMEDIATION OF POPS POLLUTED SITES IN REPUBLIC OF MOLDOVA

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### Abstract

Inventory of pesticide polluted sites in Republic of Moldova showed a huge number of high polluted sites and large pollution spectrum. The identified sites need effective remediation actions in order to diminish the risks for environment and public health. Some demonstration projects on the remediation technologies have been tested in the country.

**Keywords:** *pollution, POPs, remediation, soil*

### Introduction

The ground beneath our feet is more precious than we know. Soil provides us with 95% of our food, hosts 1/4<sup>th</sup> of the world's biodiversity and helps us combat and adapt to the changing climate. Soil chemical composition is subject to external factors such as wind, rains, evaporation.

Important pollution sources for the environment in the Republic of Moldova are old pesticides storages. The MAC (Maximum Admissible Concentration) of POPs in soil for agriculture land in Republic of Moldova is 0.1 mg/kg (Ministerul Ecologiei si Resurselor Naturale 2004). This is a very restrictive level, but it excludes the effects of pesticides bioaccumulation in crops.

The inventory of pesticide polluted sites showed a huge number of high polluted sites (near 250) and large pollution spectrum (figure 1). More than 15% of the sites were determined as extra high polluted sites where the POPs concentration is greater than 50.0 mg/kg. the pollution spectra of those territories include such chemical compounds as HCH (hexachlorocyclohexane) and DDT and its metabolites (Bogdevich et al 2016).

Effective remediation actions are needed for the polluted sites with high risk for environment and public health.

They include some of the world's most harmful chemicals, including POPs (DDTs, HCHs, Chlordane, Heptachlor, Toxaphene), PAHs (17 toxic substances), Triazines, Trifluraline, and other old pesticides. The POPs degradation and microbiological properties of contaminated soils have been investigated in the application of the phytoremediation experiment (Bogdevich & Cadocinicov 2009) and DARAMEND technology (Bogdevich et al 2013). Indices of the microbial biomass, counts of culturable microorganisms (heterotrophic bacteria, actinomycetes and fungi) and dehydrogenase activity have been determined by these experiments.

Also some laboratory tests were made for the use of carbonaceous sorbents for soil remediation.

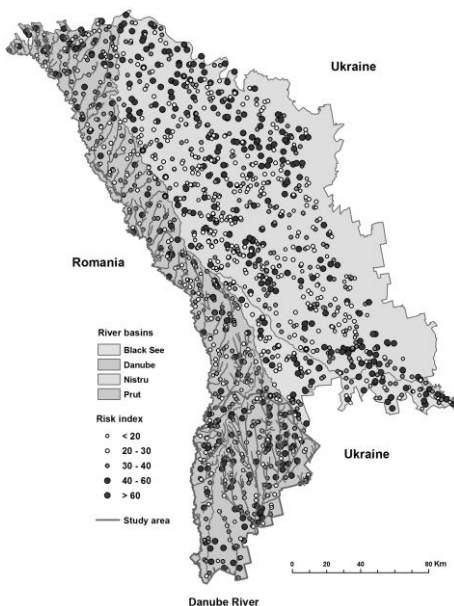


Figure 1. POPs contaminated sites in the Republic of Moldova

## Experimental

GC and GC/MS equipment and international analytical methods (EPA, ISO, etc.) have been used in the accredited by ISO 17025 laboratory for determinations of the concentration of toxic substances in different environmental samples.

Based on previous investigation of POPs polluted sites, locations for remediation experiments were selected in Balceana and Bujor, Hincesti district, for a more detailed investigation.

The concentrations of organochlorine pesticides were determined by gas chromatography (Agilent 6890 equipped with a  $\mu$ ECD detector) following the USEPA Method 8081A. The calibration interval was from 0.02 to 0.5  $\mu\text{g}/\text{ml}$ . The following pesticides or pesticide metabolites were analyzed in the samples:  $\alpha$ -,  $\beta$ -, and  $\gamma$ -HCH isomers, hexachlorbenzene (HCB), heptachlor, aldrin, dieldrin, endrin, chlordane, DDE, DDD, and DDT.

Soil samples were taken from top soil, 0 - 20 cm. The samples were air-dried under laboratory conditions of about 20°C, sieved through a 1.0 mm sieve, and homogenized. Plant samples were dried in a drying box at 60°C. 10 gram of soil subsamples and 1 - 2 g of plant tissue subsamples were extracted by Soxhlet system for 14 hours. The solvent was a mixture of hexane and dichloromethane (1:1 by volume), total volume of 150 ml.

The detection limit was 10.0  $\mu\text{g}/\text{kg}$  for DDTs, aldrin, dieldrin, endrin, and chlordane and 5.0  $\mu\text{g}/\text{kg}$  for HCHs, hexachlorbenzene, and heptachlor. The maximal admissible concentration (MAC) for pesticides in soil was considered to be 100  $\mu\text{g}/\text{kg}$  based (or 0.1 mg/kg) according to national legislation (Ministerul Ecologiei si Resurselor Naturale 2004).

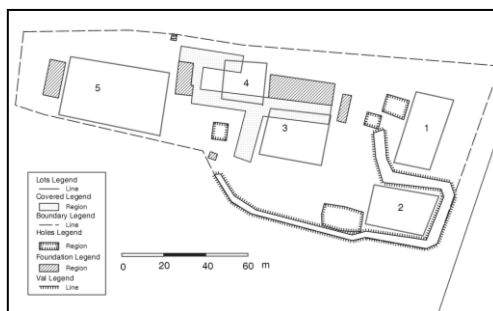
### Phytoremediation

The Balceana site was selected for the phytoremediation field experiment based on two premises (1) it is a sufficiently large cultivatable area surrounding the site, which is polluted by obsolete pesticides, primarily by DDTs and (2) the involvement of the local community for planning and conducting the study appeared to be good. The soil at the Balceana site is classified as a "chernozem" with a pH=7.6 and an organic carbon content of 3.2%. It is situated in the lower Lapusna River Valley. The depth-to-groundwater is 3.0–3.5 m. The foundation area was not used for the phytoremediation study.

The trial was managed by a local farmer chosen by competition who conformed to special requirements. This is a feasibility demonstration of managing a phytoremediation application using local expertise in cooperation with government and research institute.

Typical agricultural techniques for soil preparation and planting were used during the experiment completion. No additional soil treatments or soil amendments were used. The field experiment was designed using five different plant species: maize (*Zea mays* L.), zucchini (*Cucurbita pepo* L. var. *pepo*), pumpkin (*C. pepo* L. var. *pepo*), carrot (*Daucus carota* L.), and sorghum (*Sorghum bicolor* L. Moench).

The site plan is presented in Figure 2. Due to differences between each of the five sections, different numbers of vegetables were used in some sections.



**Figure 2.** The design of sections within the foundation area of the former Balceana pesticide storage facility (experimental sections are numbered 1–5).

Three sections were planted with three vegetables: maize, zucchini, and pumpkin. On one section all five plant species were planted and the fifth section was limited to two plant species: corn (*Zea mays* L.) and pumpkin (*C. pepo* L. var. *pepo*).

Plant part samples (roots, stems, petioles, leaves, and fruit) were taken for each species after the vegetative growth period for assessment of pesticide accumulation.

### Bioremediation

The experiment was based on in-situ bioremediation by land farming with the addition of amendments of DARAMEND® by PeroxyChem (previous Adventus) (*PeroxyChem: Daramend® Anaerobic Bioremediation Reagent* f.a.). Sequential cycles of anaerobic (no oxygen, strongly reducing conditions) and aerobic (oxygen present) conditions enhance reductive dechlorination of chlorinated organics. This solid-phase bioremediation technology employs organic and inorganic amendments

to stimulate the decomposition of organic contaminants by indigenous soil microorganisms.

5 - 10 cycles of treatment have been applied to the top soil at the demonstration site. The soil was allowed to rest for at least 5 days during the anaerobic (reductive) phase. Reducing conditions were needed to be maintained during that period to induce reductive dechlorination of DDTs and HCHs. It was achieved by ensuring that the moisture content was high by the covering the wet soil with black plastic sheeting. The soil was tilled during the anaerobic (reductive phase) to provide oxygen, and then allowed to rest without any covering or addition of water for at least two days during the aerobic phase. Two phases (anaerobic and aerobic) were repeated for each treatment cycle. Soil sampling was repeated after 5 and 7 cycles.

#### *Laboratory Sorption study*

A standard mixture of 8 chlorinated pesticides (at different concentrations- 50 and 120 ng/l) in methanol, containing: p,p'-DDT, o,p'-DDT, p,p'-DDE, p,p'-DDD, o,p'-DDD,  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH or lindane, purchased from LGC Standards was used. The internal standard (IS) containing 0.1  $\mu\text{g/ml}$  PCB29 and 0.1  $\mu\text{g/ml}$  DCB.

All standards and working solutions were stored at 4°C in glass bottles with caps. Deionized water was obtained from an Ultra Clear ultra-pure water system. Hexane, methanol of residue analysis grade was purchased from Fluka (Sigma-Aldrich, Germany).

Batch data were obtained using 100 ml samples. The tests were generally conducted by setting up a series of flasks each with the same concentration of adsorbate, but with different doses of carbon. Blanks were also used which contained no carbon. Tests were conducted by adding an accurately weighed dose of carbon to a series of 250 ml flasks containing solution of known concentration.

After adding the known concentration of adsorbate and internal standard, the flasks were placed on a shaker for overnight. After, the doses of carbon were added to each flask and they were placed on a reciprocating shaker for one hour.

After one hour, the solutions were filtered and the filtrate was used for liquid-liquid extraction. Hexane was used as an extracting solvent. Two portions of hexane each of 5 ml were used. Extracts were mixed and were evaporated to a final volume of 1 ml, which was transferred into a screw cap vial. Analytical process on GC and GC/MS Agilent 6890 system with Agilent 5973 mass detector was used for the determination of organochlorinated pesticides. The conditions of the GC-MS were as following: a HP-5MS capillary column (30 m  $\times$  320  $\mu\text{m}$  id, 0.25  $\mu\text{m}$  film thickness). The carrier gas was helium with a flow rate of 1.3 mL/min. The quadrupole temperature was maintained at 150 °C. The ionization was carried out in electron impact mode at 70 eV. The acquisition mode was SIM. Retention times and molecular ions were used as the key criteria for identification.

## **Results and Discussion**

### *Results of phytoremediation experiment*

Two plants showed a good extraction capacity for DDTs and HCHs: zucchini (C. pepo L. var. pepo) and pumpkin (C. pepo L. var. pepo). Zucchini plants were grown in three of the sections of the studied site. Each section had different initial soil DDTs concentration in the rhizosphere (from 0.12 to 4.02 mg/kg). Zucchini

accumulated a high level of DDTs and the amount of accumulation depended on pesticide concentration in the soil near each plant (Figure 3).

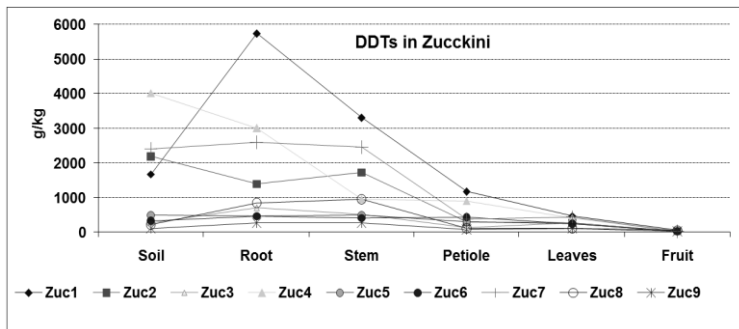


Figure 3. Total DDTs concentration in Zucchini plant parts (dry weight)

Total accumulation of DDTs decreased from the roots to the fruit. Relatively high level of accumulation was observed in the roots and stems. Accumulation in the stem is the most important result for phytoremediation because it shows translocation of DDTs from the roots to aboveground stems that are most easily harvested and removed from the site.

The pumpkin plant treatment also showed good phytoextraction capacity (Figure 4). The pumpkin biomass was greater than zucchini biomass. The length of pumpkin stems reached up to 3 – 5 m. The stems next to the plant roots showed higher concentrations of DDTs compared to stems farther from plant roots. Bioaccumulation factors (BAF) values for DDTs in plant tissues were close to the values observed in zucchini. BAF for stem concentration varied in the range of 0.45-3.01. The average decreased from 2.05 for roots to 0.82 for leaves. The fruit accumulate much lower amounts of DDTs, BAF 0.05. The weighted average value of BAF for zucchini was 1.10, and for pumpkin-1.42.

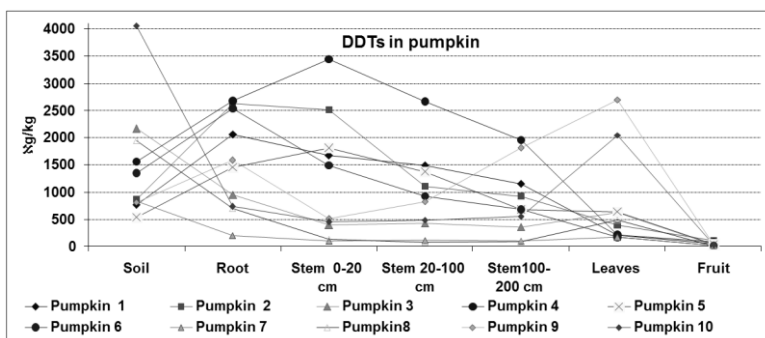
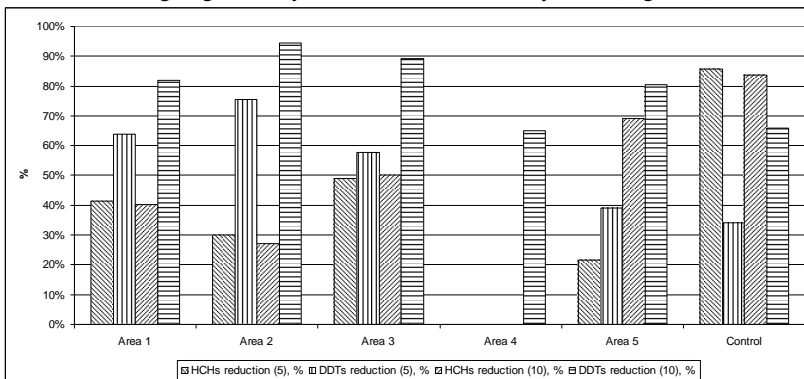


Figure 4. Total DDTs concentration in Pumpkin plant parts (dry weight)

Results of bioremediation experiment

The main soil pollutants at the experimental site were DDTs and HCHs isomers. The bioremediation of polluted soil after 5 cycles led to the decreasing of total POPs concentration in soil in the range of 22 to 86% for HCHs and of 34 to 76 % for DDTs (Figure 5).

The average POPs destruction after 10 cycles of treatment showed a higher level in comparison with 5 cycle treatment. The results after 10 cycles of treatment demonstrate appreciable reduction for DDTs (65%-82%) and HCHs (27%-42%). The destruction of studied pesticides is indicated also for control area. The HCHs concentration is going down by 86 %, and for DDTs – by 34 % (Figure 5).

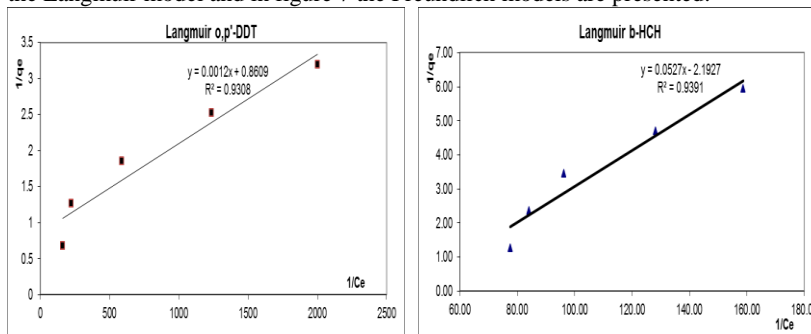


**Figure 5.** Reduction of HCHs and DDTs concentrations after 5 and 10 cycles of bioremediation experiment

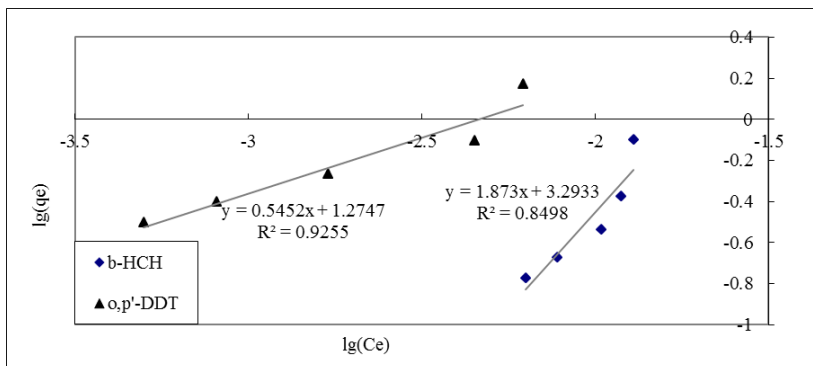
#### Results of sorption study

The results of the batch studies using commercial mix of organochlorinated pesticides showed that great majority were absorbed onto activated carbon. Such components were:  $\alpha$ -HCH,  $\gamma$ -HCH,  $p,p'$ -DDE,  $o,p'$ -DDD,  $p,p'$ -DDD,  $p,p'$ -DDT. For  $\beta$ -HCH and  $o,p'$ -DDT, a relationship between the carbon amount and the amount of the pesticide adsorbed was observed.

In the study, experimental data for  $o,p'$ -DDT and  $\beta$ -HCH were fitted to the linearized sorption isotherm models: Langmuir and Freundlich. In figure 6 data for the Langmuir model and in figure 7 the Freundlich models are presented.



**Figure 6.** The linearized Langmuir Model: a) for  $o,p'$ -DDT and b) for  $\beta$ -HCH



**Figure 7.** The linearized Freundlich Model for o,p'-DDT  $\beta$ -HCH

## Conclusions

Organic pollutants in the ecosystem, especially persistent organic pollutants (POPs) are of the most important environmental concern in the world.

The experience of the site remediation in the Republic of Moldova showed that local conditions should be determined individually for every site.

Another major factor for the remediation action is pollution spectrum. The conclusion is that possible remediation action should to be developed after the complex study of pollution spectrum and geotechnical conditions for every polluted site by the complex approach.

Phytoremediation can be used for the remediation of polluted sites; however, it needs to be designed based on site conditions. All advantages and limitations of this technology should be taken into consideration. Agricultural phytoremediation might be time consuming and could require a complex use of approaches as biotechnology for high pollution levels.

POPs degradation in composts after bioremediation was significant and fitted to the growth of the microbiological activity. The utilization of DARAMEND in most cases promotes the growth of microorganisms which can lead to pollutant destruction processes. However, POPs microbiological degradation in sites, where DARAMEND was used, showed the similar level in the comparison with background site.

Adsorption is recognized as an effective and low cost technique for the removal of organic pollutants from water and wastewater that produces high-quality treated effluent. The laboratory study highlighted the removal of different organic pollutants using adsorption technique, adjusted to local conditions. Activated carbon was obtained from local raw materials and was used for the remediation of POPs polluted soil in laboratory conditions. Results showed a good perspective for the utilization of activated carbon for the soil decontamination and agriculture site remediation.

### **Acknowledgements**

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