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PlantPower – Phytoremediation of Contaminated Soils in Former Minefields of the Western Balkan Area

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Abstract

The PlantPower project aims to the phytoremediation of explosive and heavy metal contaminated soils in the former minefields in the Danube River Basin of the Western Balkan Area, particularly in the Sava/Danube stretch in Croatia and Bosnia and Herzegovina that were seriously affected by landmines during the last Balkan War. The occurrence and chemical burden of the explosives containing xenobiotics in the soil of the cleaned minefields will be evaluated to provide data sets, which are necessary for scientifically-based risk assessment and future phytoremediation process that will be implemented in the affected areas. Based on the obtained results, special emphasis will be put on choosing the most efficient plants for phytoremediation in the defined areas as well as to the optimal and environmentally friendly waste management options for plant removal, disposal and/or re-usage after the phytoremediation. A combination of state-of-the-art methods will be applied to evaluate site contamination and to predict future usage of plant species for the phytoremediation. The PlantPower project will also generate new knowledge on environmental risks of former minefield areas, and EU regulators and policy makers will be able to make better informed decisions about future regulations of explosive affected areas.

Keywords: *Minefields, Soil, Contamination, Phytoremediation, Waste management, Sustainable development*

Introduction

Phytoremediation is technology that uses living plants, and their associated microbes, to accumulate, detoxify and stabilise contaminants in an environmentally friendly, cost-effective and sustainable way. It can be used for remediation of contaminated soil, water and air. Phytoremediation has been successfully used to detoxify large amounts of contaminants, including pollutants such as petroleum, hydrocarbons, chlorinated solvents, pesticides, radionuclides, as well as heavy metals and explosives. The process is based on plant mechanisms involving accumulation, complexation, volatilization, and degradation of organic and inorganic pollutants. This technology has gained increasing attention over the past decades largely due to its aesthetic appeal. The most important requirement for phytoremediation is usage of fast growing plants that are capable of uptake and accumulation of large amount of toxic substances in their aboveground harvestable parts (Ali et al. 2013, Barman et al. 2000, Dushenkov 2003, Hooda 2007, Lim et al. 2004, Marchiol et al. 2004, McCutcheon & Schnoor 2004, Meagher 2000, Meagher 2006, Morel et al. 2006, Nanda et al. 1995, Sharma et al. 2015, Stojanović et al. 2012, Wuana & Okieimen 2010).

Phytoremediation has been increasingly used as a sustainable approach for the remediation of contaminated sites. The costs associated with these remediation methods are usually lower than other well-known remediation technologies. Some of the environmental impacts, like atmospheric emissions and waste generation, are reduced to minimum or became non-existent. Moreover, the biomass produced in phytoremediation could be economically valorised in the form of bioenergy (e.g. biogas, biofuels or combustion for energy production and heating), representing an important environmental and economic co-benefit, added to the others, such as erosion control, improving soil quality and functionality, and increasing the safety of wildlife habitat (Bhadra et al. 1999, Bridgwater et al. 1999, Ghosh & Singh 2005, Gomes 2012, Helsen & van den Bulck 2003, Kumar 2013, Liphadzi et al. 2005, Mojiri 2011, Reichenauer & Germida 2008, Subramanian et al. 2006).

The large-scale production, processing and use of munitions and explosives lead to vast environmental pollution; especially polluted is the soil. Explosives contain toxic and mutagenic compounds such as TNT (2,4,6-trinitrotoluene), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and/or HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) that can be later on found in the polluted soil. These xenobiotics are stable in the environment and resistant to remediation. Certain technologies used so far (e.g. incineration, adsorption, advanced oxidations processes and chemical reduction) have not only been very expensive but they also caused additional environmental problems. In contrast to them, phytoremediation is relatively cheap, environmentally friendly and societal accepted solution (Harvey et al. 1990, Kiiskila et al. 2015, Mohanty 2016, Vila et al. 2007).

Landmines are one of the most environmentally destructive consequences of war leading to severe environmental damages. Disruption of land's stability, pollution and loss of biodiversity constitute major ecological repercussions of landmine crisis. The impact of landmines on soil, flora and fauna as well as people depends whether the mines have been detonated or not. The contamination itself can be delivered directly or indirectly, pollutants can leach into subterranean waters and bioaccumulate in the organs of plants causing harmful effects. Moreover, they can later on enter the food chain, so animals and humans are also endangered. (Berhe 2007, Misak & Omar 2007).

Landmines are made of metal, timber or plastic casing and filled with TNT, RDX and/or HMX. They can also introduce other non-biodegradable and toxic waste, such as depleted uranium and some heavy metals such as iron, manganese, zinc, chromium, cadmium, nickel, copper, lead and mercury. These compounds have been known to leach into the soil and underground water during mines disintegration. Many of the organic and inorganic substances and compounds that are derived from the explosives are long lasting, water-soluble and toxic even in small amounts. The main harmful characteristics of those compounds are mutagenicity, carcinogenicity, and harmful effects on reproductive systems, congenital defects, skin irritation and disruption of the immune system (Abadin et al. 2012, Berhe 2007, Talmage et al. 1999). Hence, this project aims to develop and conduct phytoremediation plan for explosive contaminated soil in former minefields.

The Western Balkan Area contains Europe's biggest minefields. Millions of landmines and other unexploded objects are lying in former war zones in South-East Europe. The most affected are Croatia and Bosnia and Herzegovina (BiH) due to the war that ended two decades ago (Bajic et al. 2015, Siljkovic et al. 2011).

The Republic of Croatia is now a mine-safe country in the sense of safety of the traffic infrastructure, tourist destinations, and areas of reconstruction, house yards and areas around the facilities of different social purposes. A Mine Information System (MIS) was developed and adjusted to complex demining procedures and implementation of public procurement and quality control processes of technical survey and demining. The size of mine suspected area (MSA) in the Republic of Croatia is 437.80 km2. MSA is also contaminated with large number of un-exploded ordinances, especially in the areas of combat operations during the war. 92.6% of the suspected hazardous area is covered by forests, 7.1% is agricultural area and other areas contribute with 0.3% (Fig 1A).[1]

Bosnia and Herzegovina are still one of the most mine contaminated countries in South East Europe; with a mine suspected area extension of 1,091 km^2. Micro-locations contaminated with mines affect the safety of 15% of the total population of BiH (Fig 1B). Current size of suspected hazardous area on cluster munition in BiH is 7.31 km^2, of which 4.3 km^2 is suspected both on mines and cluster munition. [2]

Hence, the overall project goal is to use phytoremediation for explosive-contaminated soils in the former minefields in the Danube River Basin of the Western Balkan Area, particularly in the Sava/Danube stretch in Croatia and BiH.

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[1] Clear and precise insight into the current status of mine suspected area and marking situation can be found at MISportal available at: https://misportal.hcr.hr.

[2] In the database (BHMAIS) it is currently registered 20,220 minefields with records available at: http://www.bhmac.org.

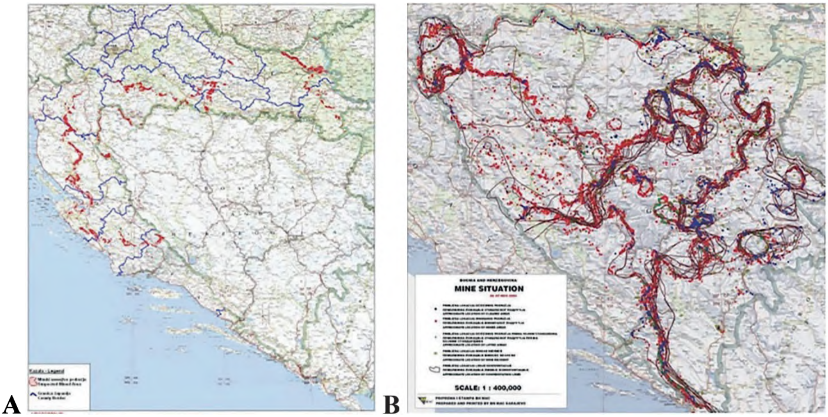

Figure 1. Mine suspected areas in Republic of Croatia and Bosnia and Herzegovina. (sources: https://www.hcr.hr and http://www.bhmac.org.)

Added value for the society/science

The PlantPower project will be implemented in the Danube River Basin of the Western Balkan Area, particularly in the Sava/Danube stretch in Croatia and BiH. The project results and findings can also be extended to any other affected area bearing in mind the nature of the pollution as well as plant species to be used in different environmental niches. The project will also inform and significantly increase awareness of local communities, agricultural workers, industry, small and medium-sized enterprises (SMEs), selected authorities and stakeholders on the issues of environmental remediation in previously contaminates areas. Project will also provide evidence-based arguments for future recommendations and regulations, in that manner promoting the ecological and sustainable development of the selected parts of designated countries, with the possible extension to the areas with similar problems within the regions of interests.

Competences of the team

Variety of expertise is required due to very different phases and processes in the course of the project. An interdisciplinary and transdisciplinary approach is indispensable, mainly because each step is entirely designed and planned according to the previous one. For the selection of the suitable area and soil sampling geographers and geologists are necessary. All soil and plant analysis, before, during and after the phytoremediation, will be performed by scientists with expertise in chemistry, biochemistry and toxicology, each of them being in charge of specific analysis during the project. Biologists, ecologists and agronomists will be leading the phytoremediation procedure; preparing the soil, choosing appropriate plants and monitoring the growth progress. Advice from public relations, economics and law will be required too, in order to control projects financials, marketing and outsourcing contracts. Their expertise will be supplemented by an advisory group consisting of experienced scientists from both academia and industry.

Project aim and objectives

Clear overall aim

- The overall project goal is to adapt phytoremediation process for explosive and heavy metal contaminated soils in the former minefields in the Danube River Basin of the Western Balkan Area; particularly on the Sava/Danube stretch in Croatia and Bosnia and Herzegovina with the future aim of restoring previous agricultural sites and subsequent revival of the rural areas.

Project objectives

- Localization of minefields in the Western Balkan Area which are appropriate for the sample collection.
- Evaluation of the occurrence and chemical burden of the explosive residues and heavy metals in the soil in previously cleaned minefields.
- Choosing or developing adequate phytoremediation procedure for contaminated soil based on the result of physico-chemical analyses.
- Choosing optimal and environmentally safe waste management options for plant removal, disposal and/or reuse after the phytoremediation process based on the toxicological analyses.

Distribution of tasks (work packages)

WP1 - Project management including time schedule, feasibility and project cost estimation

The WP1 is dedicated to the project management. The objectives are a) ensuring a high standard of supervision and overall administration, quality control and coordination of research tasks described in WPs 2-8; b) supervision of all partner-related issues; c) providing financial management, coordination based on the rules and guidelines of the financing agency, and d) setting up a framework for communication and managing communication flow among different partners and stakeholders in the frame of the project.

The assessment of the feasibility of the study has been done in 5 aspects to evaluate the project's potential for success. 1) Technical feasibility - assessment is centred on the technical resources available for the organization. Technical and scientific aspects have been evaluated and described in WPs 2-7; 2) Economic feasibility - costs associated with projects estimated for financial resources allocation; 3) Legal feasibility - investigations have been done to verify if the proposed system conflicts with legal requirements. 4) Operational feasibility - a study has been done to determine whether the functional needs can be fulfilled. Hiring a subcontractor is suggested after first cycle of planting; 5) Schedule feasibility is the most important for project success. This study has been done for one cycle of planting.

According to Figure 2, the critical path of the Gantt chart will need 5 years to be accomplished. The schedule was made for one cycle of phytoremediation and the next strategies will be planned according to the results of the first cycle. Time schedule is based on the example of phytoremediation by sunflower within the period of 1.5 year (the selection of the specific plants will be based on the results from the WP3 in the first step of WP4).

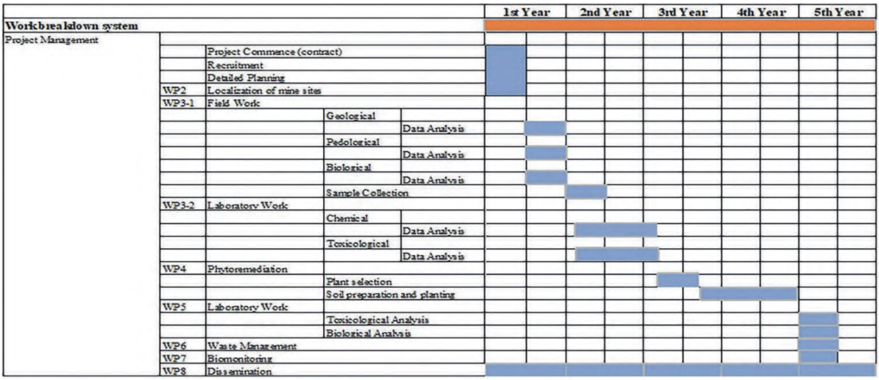

Figure 2. PlantPower project timeline with defined work packages (WPs).

WP2 - Localization of mine sites for phytoremediation process in Croatia and Bosnia and Herzegovina

The objective of WP2 is to create a detailed database, based on the already available information from HRC and BHMAC (sources: https://www.hcr.hr and http://www.bhmac.org), on the temporal and special distribution of former minefields in the Danube River Basin of the Western Balkan Area, particularly on the Sava/Danube stretch in Croatia and BiH that are appropriate for future phytoremediation. Minefields suitable for phytoremediation will be chosen according to the possibility of their usage for agricultural purposes. Data regarding cleaned minefields will be regularly updated by the participating project partners.

WP3 - Soil sample collection and quantitative chemical analysis of explosives and heavy metals in soil samples in designated areas of Croatia and Bosnia and Herzegovina

The objective of WP3 is to collect soil samples and perform quantitative analysis. Soil sampling is a basic step for decision making about the proper plants that will be used for phytoremediation. Sampling will be done according to ISO 18400-102:2017 guidelines and sampling methods will be selected based on soil types according to the available data for the soil classification in Croatia and BiH. Before taking the samples, the demined fields in designated areas must be carefully inspected. Field observation includes geological, pedological and biological data collection. Since RDX contamination can spread more deeply into the soil and has a superior ability to leach into water resources, the sampling should be done in topsoil near surface and in greater depths. Afterwards, bio-physico-chemical characterization of the soil will be conducted to determine and to quantify existing pollutants according to ISO/TC 190/SC 3. After determining occurrence of chemicals of interest, their metabolites and transformation products, they will be classified according to their chemical structure and/or mechanisms of action. For the quantitative chemical analysis highly sensitive methods will be used. Preparation of samples will include different physico-chemical procedures, such as centrifuging, filtration, homogenisation, and extraction; the detection of explosives and heavy metals will be done with highly sensitive and specific methods, gas and liquid chromatography with DAD and MS detectors (GC-MS, LC-MS, and HPLC-MS).

WP4 - Phytoremediation process of contaminated soil in designated areas of Croatia and Bosnia and Herzegovina

The objectives of WP4 will be targeted to adaptation of phytoremediation process of contaminated soil in designated areas of Croatia and BiH. Phytoremediation will be used since it is regarded as potentially the least harmful revitalisation method. It uses autochthonous organisms and preserves the environment in a natural state. Main advantages are easy monitoring and the possibility of the recovery and re-use of valuable metals. The lower cost of this technology makes it affordable especially in lower-income countries.

Plants used in phytoremediation are well known and safe for the biosphere, only autochthon species will be used; some of the possible plants would be crops that are commonly used in the region. Semi-natural landscape provided by the plants can support the societal acceptance of this technology. Main interest of the planned phytoremediation would be leftovers of heavy metals and explosives from the mines and bombs used during the war, because of their high toxicity and carcinogenicity. Plants applied in the phytoremediation process will be chosen based on the results of the soil contamination gained after laboratory work described in WP3. Both the physico-chemical properties and contamination of the soil will be taken into the account during plant selection process. Accumulating plants that are suitable for the targeted area are shown in the Table 1.

Table 1. Accumulating plants suitable for the targeted region

Heavy metals *(As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Sr, Zn)*	*Corn (Zea mays), sunflower (Helianthus annuus), oil rape (Brassica napus), edible rape (Brassica chinensis), soybean (Glycine max), tobacco (Nicotiana sp.), alpine penny-cress (Thlaspi caerulescens), Indian mustard (Brassica juncea)*
Radioactive elements *(U)*	*Sunflower (Helianthus annuus), tobacco (Nicotiana sp.), edible rape (Brassica chinensis)*
Explosives and their metabolites *(TNT, RDX)*	*Corn (Zea mays), Arabidopsis sp. (A. arenosa, A. croatica, A. halleri, A. thaliana), soybean (Glycine max)*

WP5 - Quantitative chemical analysis of explosives and heavy metals in plant material after each cycle of phytoremediation

The main objective of WP5 is to generate a quantitative chemical analysis of explosives and their metabolites as well as heavy metals in different plant tissues after phytoremediation process in order to identify the level of plant contamination. This will be done according to well-established methods and OECD guidelines for the testing of chemicals in terrestrial plants. Detection methods will be the same as mentioned in WP3. Data obtained by those analyses will facilitate a selection of waste management options or possibilities of re-use of certain plants based on their contamination burden.

WP6 - Waste management options after plant removal from designated areas of Croatia and Bosnia and Herzegovina

The objective of WP6 is to choose appropriate waste management option for the harvested plants after the phytoremediation. This will be done according to the well-established methods and specific guidelines, paying distinguished attention to the local environment. The volume and dry weight of harvested plants can be reduced by composting and compaction, but further treatment is needed in both cases due to the high concentration of accumulated toxic pollutants (heavy metals, metabolites of explosives and radioactive substances).

Compacted material can be completely demolished by pyrolysis or reused in process of combustion and gasification. In these procedures biomass is burned under controlled conditions, so bioenergy or biofuels are produced. By applying combustion, the volume of harvested plants can be reduced to 2-5% of the initial value; however, the ash should be handled properly. Possibilities for reusing heavy metal content of the combustion residual are already defined with the alternative possibilities related to cost-effective feasibility that will be explored in the frame of WP6.

Outsourcing part of the waste management process is advised according to requirements such as feasibility study, necessity of special equipment, skilful manpower, transportation facilities, legal restriction etc.

WP7 - Biomonitoring of contaminated soil in designated areas of Croatia and Bosnia and Herzegovina after phytoremediation cycle

The main objective of WP7 is a repeated biomonitoring of contaminated soil from former minefields in designated areas after phytoremediation cycle. The biomonitoring will be carried out to evaluate efficiency of the applied phytoremediation and to provide data about the outcome of soil remediation. Detailed quantitative chemical analysis will be done according to the methods already mentioned in the frame of WP3.

WP8 - Outputs/Dissemination

The WP8 is aimed to disseminate the project results a) to the interested parties, relevant stakeholders and policy makers; b) with the academic and research community interested in the topics addressed by the project and stimulate further research in the field; and c) through various media. The dissemination actions goals will be achieved through preliminary dissemination actions that include the selection of specific project logo, the setup of a common webpage, press releases, and the development of promotional and informational materials such as newsletters, brochures, leaflets and articles in mass media. Scientific dissemination will be done by means of scientific papers, conference presentations, and dissemination of relevant results to public and stakeholders, such as agricultural workers and policy makers. Scientific papers will be published in the domain of Agricultural Engineering, Agricultural Economics & Policy, Agronomy, Biotechnology & Applied Microbiology, Ecology, Environmental Sciences, Environmental Studies, Green & Sustainable Science & Technology, Plant Sciences, Public, Environmental & Occupational Health, Soil Science and/or Toxicology according to the categories given by Journal Citation Reports. Dissemination events will be conferences, seminars and workshops.

Long-term outputs and contributions

- Contribution to risk assessment of minefields pollutants, with special attention to human health and sustainable ecosystem.

- Contribution to the protection of citizens and wildlife from adverse effects through the strengthening of national mechanisms for surveillance and response to health threats.
- Contribution to legal framework amendment regarding to the environmental and health safety norms.
- Contribution to specific legislation on soil protection including Soil Thematic Strategy (COM (2006) 231) and the Seventh Environment Action Programme, recognising that soil degradation is a serious challenge.
- Contribution to the rural development and revival of the rural areas.
- Contribution to the relevant EU and national bodies, policies and strategies.

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