Tamara Jakovljević[1*], *Ivana Radojčić Redovniković*[2], *Anamarija Laslo*[1]

[1]*Croatian Forest Research Institute, Jastrebarsko, Croatia,*
[2]*University of Zagreb, Faculty of Food Technology and Biotechnology, Zagreb, Croatia*

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Phytoremediation of heavy metals - Applications and experiences in Croatia

ABSTRACT

Phytoremediation is defined as the effective use of plants to remove, detoxify or immobilize contaminants in the area of growth (soil, water, sediment) through biological, chemical or physical processes naturally occurring in plants. It involves growing plants in a contaminated medium, over a certain period of growth, in order to remove contaminants from the medium, or to facilitate the immobilization (binding/stopping) or degradation (detoxification) of contaminants. The biggest problem are inorganic contaminants, as opposed to organic, they are not biodegradable to less or nontoxic compounds. The main representatives of inorganic contaminants are heavy metals which pollute soils and introduce hazardous effects to the environment and to animal and human health. A large number of researches indicates that plants have a huge genetic potential that allows the removal of toxic metals from the soil, so they may play a major role in the process of phytoremediation. A research has been carried out in Croatia in this regard, related to which kind of plants are best suited to facilitate the process of phytoremediation and results showed that poplar (Populus sp.) had the highest tolerance to heavy metals and highest prospect for successful application in phytoremediation.

Keywords: *phytoremediation, contaminants, heavy metals, plants, poplar.*

1. INTRODUCTION

Industrialization, environmental disasters, inadequate waste disposal are some of the major sources of largest and still growing global problems of our time - environmental pollution. The biggest problem are inorganic contaminants, as opposed to organic, they are not biodegradable to less or nontoxic compounds [1]. The main representatives of inorganic contaminants are heavy metals. Heavy metals and metalloids have increasingly become subject of interest of many researchers in the scientific disciplines today. The reason for this is their ubiquity and significant, yet insufficiently known effects on wildlife [2]. Lead (Pb) is one of the most common heavy metals present in the soil. Increased concentration of lead may cause loss of vegetation, and it displays the genotoxic effect [3].

Today, the biggest challenge is finding the most appropriate methods for the restoration of contaminated areas. Precise remediation of areas contaminated with heavy metals is especially demanding [4]. Traditional physical-chemical methods of removing heavy metals are often expensive, hardly feasible and inefficient, also, such techniques can disrupt the structure of the soil and its agricultural or urban reuse [5]. Ecologically and environmentally sound solution provides a new biotechnological process of phytoremediation, which is based on the ability of plants to clean and restore the contaminated area. A large number of researches indicates that plants have a huge genetic potential that allows the removal of toxic metals from the soil, so they may play a major role in the process of phytoremediation [4]. As such a process, phytoremediation is environmentally and visually acceptable, inexpensive, and offers the possibility of bioremediation of soil. There are two methods of phytoremediation of soil contaminated with metals, both of which are designed to reduce the bioavailability of metals; phytoextraction and phytostabilization. Phytostabilization is not a pro-

*Corresponding author: Tamara Jakovljević
E-mail: tamaraj@sumins.hr
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cess of elimination, but stabilization of trace elements that are potentially toxic. This process gains greater control by increasing the stability of the soil and by preventing the spread of contamination, with a pleasant appearance and reduced cost, compared to some methods [4].

Despite the great potential, phytoremediation yet has to become commercially available method. Research which studies the effects of increased concentration of the lead and which aim is to identify sustainable methods for removing or immobilization of lead in the soil by trees has been receiving increased attention in the last few years because of the negative consequences of high concentration of lead on plants [6]. Furthermore, special attention was given in the past decade to development of phytoremediation procedures using trees, due to a number of positive characteristics, such as rapid growth, high biomass, deep root system, visually unimposing appearance and low-cost of maintenance. All theese benefits draw more attention to trees as a potential choice for phytoremediation [7].

Phytoremediation, as a generic term for various technologies, is defined as the use of vegetation in decomposition, accumulation, separation, stabilization of inorganic and organic contaminants in soil, sediment, surface water and groundwater [7]. Inorganic contaminants that can be naturally present in the earth's crust or atmosphere, however, their increased concentration is the result of human activity (such as mining, industry, transport, agriculture and military activities) and has a toxic effect. The organic pollutants often have anthropogenic origin, they are toxic and have carcinogenic effect [8]. Unlike organic contaminants, inorganic contaminants are not biodegradable and they been accumulate and stabilized in different parts of the plant [1].

Phytoremediation can be defined as the effective use of plants to remove, detoxify or immobilization of contaminants in the area of growth (soil, water, sediment) through biological, chemical or physical processes naturally occurring in plants. Plants are unique organisms, which have developed various defense systems due to the inability of changing habitats, in order to ensure their survival. The plants have well-developed absorption and metabolic capabilities, as well as transportation systems that can selectively enter different nutrients and compounds directly from the medium in which growth (water, soil). Phytoremediation involves growing plants in a contaminated medium (soil, water), over a certain period of growth, in order to remove contaminants from the medium, or to facilitate the immobilization (binding / stopping) or degradation (detoxification) of contaminants. Plants can be collected, processed or disposed of as waste after a certain period [9].

The method of remediation of polluted environment by plants is a passive technology that can be used in places of low, medium or moderate levels of pollution. More complex contaminated areas often used different methods of remediation using plants, thus improving the efficiency of purification and increasing the potential remedial effect of plants [10]. Phytoremediation is an alternative or complementary technology that can be used together with conventional mechanical cleaning methods, which often require high capital investment and a lot of manpower and energy. Such mechanical technology can completely replace phytoremediation [11]. Depending on the underlying processes, the applicability and the type of contaminant remediation of plants can be categorized as:

1. Phytodegradation – utilization of plants for absorption, storage and degradation of organic pollutants trough reaction of plant enzymes within the plant tissue
2. Rhizodegradiation - utilization of a symbiotic relationship between plants and micro-organisms to decompose organic contaminants in the rhizosphere
3. Phytovolatilisation - utilization of plants' ability to absorb the contaminant from the media and remove it translate into less or no harmful gaseous form
4. Phytoextraction - utilization of plants for absorption and storage of toxic contaminants from the medium in different plant tissues
5. Rhizofiltration - utilization of ability of plant roots to absorb and store contaminants from aqueous media
6. Phytostabilisation - reduction of mobility or binding of contaminants in the plant root zone, thereby reducing their mobility and availability

This categorization is showed in Figure 1.

Phytoremediation is an *in situ* remedial technology which use natural, living plants inherent processes, it is environmentally friendly, powered by solar energy and is based on the concept of using nature to clean nature [13]. However, like all technologes, it has its advantages and disadvantages. Early research shows that phytoremediation technology is promising solution for cleaning pollutants and polluted areas, but with certain restrictions. Figure 2. shows some of the advantages and limitations of phytoremediation. Many of the advantages and limitations of phytoremediation are direct consequence of the biological aspect of this type of purification system [14].

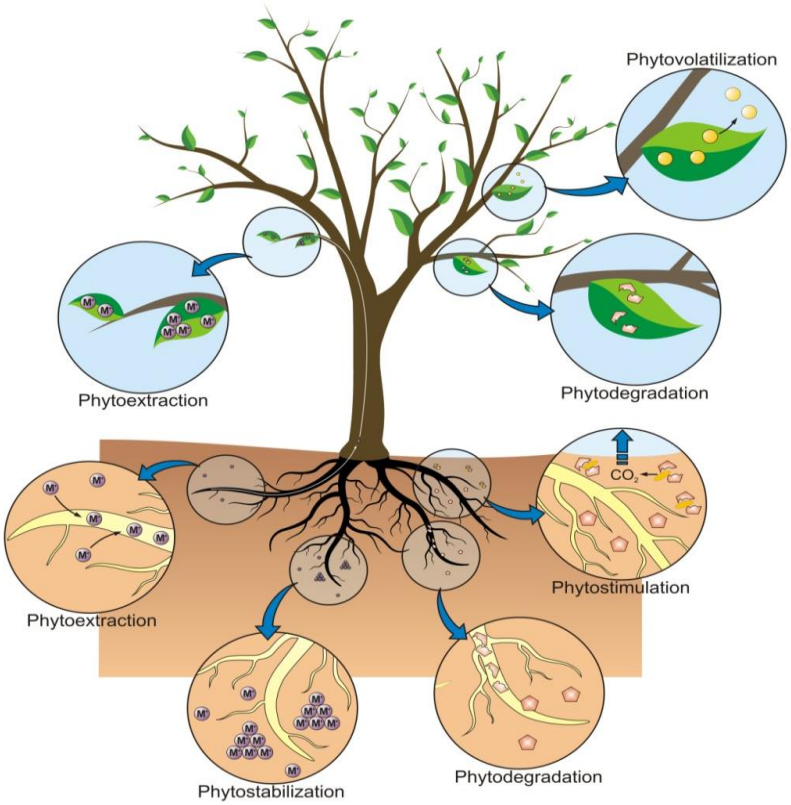

Figure 1 - Types of phytoremediation [12]

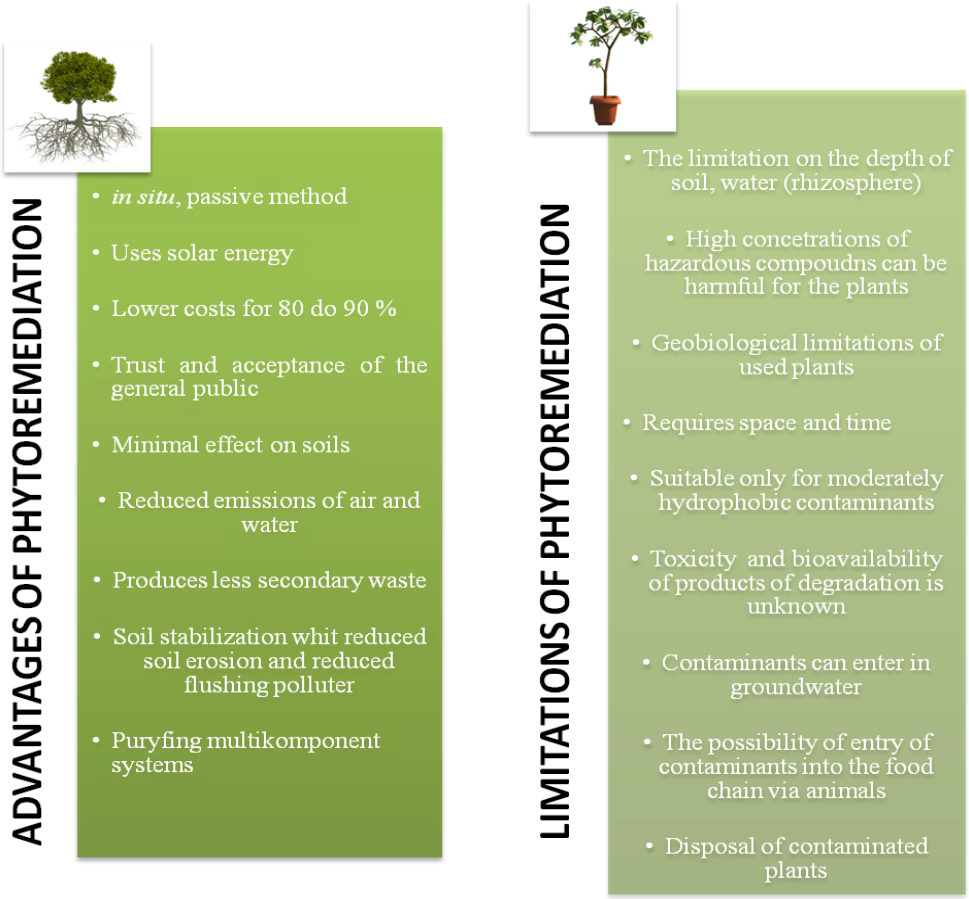

Figure 2 - Advantages and limitations of phytoremediation [15]

2. DISCUSSION

One of the biggest current problems in modern ecology and agroecology is soil contamination caused by heavy metals. According to the conducted research, total amount of heavy metals in all counties is higher in soils of urban areas, nearby industrial facilities and oil and gas wells, than in areas of intensive agricultural production. The above statement is confirmed by research impacts on soil pollution with heavy metals and annual quantities of heavy metals introduced into the soil mineral fertilization [16].

The term "heavy metal" usually refers to the chemical elements whose relative density is greater than 5.0 g cm^{-3}, which are metals or metalloids that have a toxic effect and that are classified as a main inorganic pollutant, but also include elements that are required by organisms in low concentration or microelements [1]. These metals are classified as essential trace elements and include metals such as copper (Cu), iron (Fe), manganese (Mn), zinc (Zn), molybdenum (Mo), nickel (Ni) and cobalt (Co). Essential trace elements in low concentrations are necessary for normal growth and development of the plant, while increased concentrations may be toxic for the plant. There are also metals which have no known physiological activity in the body or are potentially toxic. Such metals are classified as non-essential elements. Non-essential elements include cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg) and arsenic (As) [17].

Examination of concentrations of heavy metals in the Nature Park Velebit, Biokovo, Učka, Lonjsko polje and Medvednica indicated a high to very high level of soil contamination with lead (Pb) [18]. Increased concentrations of lead (Pb), copper (Cu), zinc (Zn) and cadmium (Cd) have been found in the areas of lowland forests of central Croatia. The cause of the increased concentrations of those metals is probably leaching from treated agricultural land [19].

According to the data available, soil of the metropolitan area is significantly more burdened by pollution and increased concentrations of lead and other heavy metals in relation to the soil in forest ecosystems due to proximity of major roads, i.e. pollution from local sources. Level of pollution of soil in Zagreb metropolitan area with lead and other heavy metals can be assessed as environmentally unfriendly [19].

The complete system for monitoring and storing data on the state of the soil has not been established. Existing data relate mainly to agricultural and forest soils. Collected soil samples were analyzed using various analytical methods, most often in the context of scientific research projects and studies, to the different needs of the target institution or, in the case of contaminated soil, for planning and implementation of rehabilitation as a result of environmental incidents. Status analysis of heavy metals in soils in Croatia has been made on the basis of studies of geochemical characteristics of soils and spatial variability of the content of potentially toxic elements in agricultural soils of Croatia. Data on the content of elements in soils was collected on 1 382 locations in different areas of Croatia. Field work was conducted in several sampling periods, mostly in the period from 2006. to 2008. and it was conducted as a systematic research where standardized methods were applied. Most part of the research covered areas and soil used for agriculture, although part of the work was done on areas that have other uses - forests, abandoned and uncultivated land, urban soils and other [20].

As for now there are no regulations governing the limits of heavy metals for different purposes of land use, however, Rule book on regulation of protection of agricultural land from pollution by harmful substances in the Republic of Croatia is currently used, which defines permissible content of harmful substances in the soil, organic fertilizers and substrates used for fertilization and increase soil fertility. Most of the samples where maximum concentration exceeds permitted values by several tens of times on agricultural land, were found in the continental area, mostly in the urban area of the city. Considering the average value of metal content in their separate regions, then the area of Istria and Kvarner islands show maximum deviation for all tested potentially toxic elements. The smallest deviation and the lowest average concentrations were found in Dalmatia and on the islands of Adriatic sea [21].

Most common specie of trees in Croatia that are used in research related to the processes of phytoremediation is poplar (*Populus* sp.). In conducted research Poplars (*Populus nigra* var. italica) was, during the 55-day growing in soil, exposed to different proportions of mass fraction of cadmium in soil (w = 10, 25, 50 mg kg^{-1} dry matter content of the soil). With a view of determining the level of accumulation and distribution of cadmium in Poplar, there were determined mass fraction of cadmium in certain parts of the plant (leaf, stem, root). The accumulation of cadmium in biomass plants increased proportionally with the increase in weight of cadmium in the soil. Distribution of cadmium in species *Populus* spp. is reduced in the following order: root> stem> leaf. Obtained results show that poplars have high tolerance to heavy metals and possibility of successful application in phytoremediation. Certain values for bioaccumu-

lation factor and for translocation factor clearly show that Poplar can be considered as a species with the potential for phytoextraction of soils contaminated with cadmium mass fraction of cadmium of 10 mg kg^{-1} dry matter content of the soil [22]. Some other studies were conducted on herbaceous species, in the area of Varaždin, the researches where conducted on dandelion (*Taraxacum officinale* agg.), ribwort plantain (*Plantago lanceolata* L.) and white clover (*Trifolium repens* L.) [23]. Also, in the area of Vinkovci, particular on the lower course of the river Bosut, the degree of eutrophic waters of the river Bosut and phytoaccumulation of heavy metals and phosphorus in the native population of duckweed (*Lemna* sp.) is been investigated [24]. Since areas classified as critical with regard to the content of cadmium exist in Croatia, obtained results from mentioned researches could serve as a solid ground for future planning and remediation of such areas.

3. CONCLUSIONS

Phytoremediation is a low-impact, *in situ,* clean up procedure that has minimal environmental disruption and practical large-scale applicability. This technology uses plants exclusively or in combination with embedded microorganisms, to degrade, contain or stabilize broad range of environmental contaminants in soil, water, and air. The main goals of optimizing the phytoremediation efficiency is the use of plants able to tolerate and accumulate high concentrations of heavy metals, in combination with the production of a great quantity of biomass. Despite several advantages, phytoremediation has not yet become a commercially available since the removal process is rather slow with lower efficiency as compared to many other techniques. To overcome these problems various biological, chemical, physic-chemical and genetic methods are used. Furthermore, multidisciplinary research in fields of trees biology, soil chemistry, microbiology and environmental science is required in order to exploit full potential of phytoremediation as a sustainable green technology.

In Croatia there is still a large number of non minig areas but also the cleared land. Much of these areas are agricultural areas for which due to mining activities there is a real danger to the increased concentration of heavy metals in the soil. In order to exploit the economic potential of these areas, and also the protection of human and animal health, phytoremediation may represent a technology of great significance, which makes the testing of autochthonous plant species with the ability of phytoaccumulation extremely important.

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IZVOD

FITOREMEDIJACIJA TEŠKIH METALA - PRIMENE I ISKUSTVA U HRVATSKOJ

Fitoremedijacija se definira kao učinkovito korištenje biljki za uklanjanje, detoksikaciju ili imobilizaciju onečišćenja u području rasta (tlo, voda, sedimenti) putem bioloških, kemijskih ili fizikalnih procesa koji se pojavljuju prirodno u biljkama. To uključuje biljke koje brzo rastu iz onečišćenog medija tijekom određenog razdoblja rasta, kako bi se uklonili kontaminanti iz reakcijske smjese, ili se olakšala imobilizacija (vezivanje/zaustavljanje) ili degradacija (detoksikaciju) zagađivača. Najveći problem su anorganski zagađivači koji za razliku od organskih nisu biorazgradivi na manje ili netoksične spojeve. Glavni predstavnici anorganskih zagađivala su teški metali koji zagađuju tlo i mogu imati opasne posljedice na okoliš, životinje i ljudsko zdravlje. Velik broj istraživanja pokazuje da biljke imaju ogroman genetski potencijal koji omogućava uklanjanje toksičnih metala iz tla, tako da one mogu igrati važnu ulogu u procesu fitoremedijacije. Istraživanje je provedeno u Hrvatskoj, a u odnosu na to koja je biljna vrsta najpogodnija kako bi se olakšao proces fitoremedijacije, i rezultati su pokazali da je topola (Populus sp.) imala najveću toleranciju na teške metale i najviše izglede za uspješnu primjenu u fitoremedijaciji

Ključne reči: *fitoremedijacija, kontaminanti, teški metali, biljke, topola*

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