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Source / Izvornik: **Poljoprivreda, 2020, 26, 30 - 42**

Journal article, Published version

Rad u časopisu, Objavljena verzija rada (izdavačev PDF)

<https://doi.org/10.18047/poljo.26.2.4>

Permanent link / Trajna poveznica: <https://urn.nsk.hr/urn:nbn:hr:151:744848>

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Download date / Datum preuzimanja: **2025-01-23**



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The remediation of agricultural land contaminated by heavy metals

Remedijacija poljoprivrednoga zemljišta onečišćenog teškim metalima

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Poljoprivreda/Agriculture

ISSN: 1848-8080 (Online)

ISSN: 1330-7142 (Print)

<https://doi.org/10.18047/poljo.26.2.4>



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THE REMEDIATION OF AGRICULTURAL LAND CONTAMINATED BY HEAVY METALS

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Scientific review
Pregledni znanstveni članak

SUMMARY

The presence of heavy metals in an agricultural land is the primary cause of food product toxicity of a herbal and animal origin associated with a contaminated agricultural land. The anthropogenic sources of pollution, especially the fertilizers and pesticides in agriculture, are the primary sources of agricultural land contamination with heavy metals. The heavy metals whose monitoring is prescribed by the current legislation of the Republic of Croatia include cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn). The aim of this paper is to provide a review of heavy metals that cause contamination of an agricultural land, as well as a review of remediation technologies applied to reduce contamination. Furthermore, the paper considers three groups of remediation technologies, i.e., the biological, chemical, and physical ones, analyzing the applicability, efficiency, cost-effectiveness and accessibility in Croatia to encourage their wider implementation. The biological remediation technologies, also known as phytoremediation, met the set criteria the most, which currently renders them most applicable to the mildly- and moderately-contaminated agricultural land. The chemical and physical remediation technologies are generally more suitable for the remediation of a severely contaminated agricultural land, applied individually or in combination with the phytoremediation methods due to the high cost.

Keywords: heavy metals, soil contamination, anthropogenic contamination, remediation technologies, phytoremediation

INTRODUCTION

The property of bioaccumulation, as a continuous accumulation of heavy metals in the body, renders the heavy metals dangerous to the human health, but also to the environment as an entity (Amari et al., 2017). The heavy metals' toxicity in organisms is caused by the replacement of certain minerals in the organic compounds with heavy metals (Jaishankar et al., 2014). Some of the possible consequences of heavy metals on human health include a damage to the vital organs and an increased cancer risk (Ludwig, 1994). Although some of the heavy metals are essential in living organisms, such as cobalt, copper and zinc, their presence in larger quantities poses a danger to the organism and a concern for the environment (Nagajyoti et al., 2010). According to Tiller (1989), a contamination of agricultural land caused by heavy metals is transmitted to the environment according to the soil-plant-animal-human system.

This results in human exposure to the contaminants by consuming the food products of a herbal and animal origin. The main contamination sources of agricultural land by heavy metals on a global scale can be divided into the natural and anthropogenic ones. The anthropogenic sources of contamination in agriculture are the primary source of emissions of arsenic, cadmium, copper, lead and zinc into the environment (Ross, 1994). Nriagu (1979) stated that 89.8% of agricultural land contamination by cadmium, 75.7% by copper, 64.4% by nickel, 94.9% by lead and 87.6% by zinc are anthropogenic. Recent studies proved that this concern is present in

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Croatia, causing soil contamination with copper in vineyards due to a copper-based fungicide (Miloš and Bensa, 2019), as well as a copper and zinc soil contamination due to various anthropogenic agricultural activities (Ružičić et al., 2019). The consequences of an agricultural land contamination are visible in the contaminated vegetables in Croatia either due to a fertilizer or pesticide application (Stančić et al., 2016) or in the form of an indirect agricultural land contamination caused by outer factors (Jurić et al., 2017). To protect the agricultural land from contamination and degradation, the Ordinance on the Protection of Agricultural Land from Contamination (*Official Gazette*, 2010) prescribes the measures to prevent and control the contamination of agricultural land by heavy metals, using various remediation technologies. This enables the maintenance of agricultural land in a condition that makes it favorable for a sustainable production of healthy food, protection of human health, and the preservation of nature and the environment. The main goal of all remediation technologies is a permanent remediation of soils contaminated by heavy metals, whereby they become environmentally acceptable for the organisms associated with the soil and the food produced on it (Martin and Ruby, 2004). Many authors (Khalid et al., 2016; Song et al., 2017) have divided the remediation technologies for a soil contaminated by heavy metals into three basic groups: a biological, chemical, and physical one. The existing remediation technologies, in addition to the positive impact on the environment as an entity, also have certain disadvantages, such as a time inefficiency, high costs of chemicals, high energy consumption and a possible secondary pollution and soil degradation (Xu et al., 2019). The costs of the potential application of remediation technologies for the treatment of various types of contamination at the European Union (EU) level annually amount to over € 17 billion, which indicates the extent of heavy metal pollution in the EU (Tóth et al., 2016). The present soil remediation management strategies in Croatia should be improved to satisfy the current EU regulations, primarily in terms of an inventory of contaminated soils and the available remediation technologies (Pilaš and Bakšić, 2014).

The aim of this paper is to provide a review of forms and sources of an agricultural land contamination by heavy metals, as well as a review of soil remediation technologies analyzed according to the applicability, cost-efficiency, and accessibility in Croatia.

HEAVY METALS CAUSING AGRICULTURAL LAND CONTAMINATION IN CROATIA

Heavy metals in an agricultural land are considered contaminants based on four conditions: (1) they remain in the soil after an impact is exerted by a contamination source, (2) they have a higher concentration in the contamination source compared to their concentration in the uncontaminated part of the environment, (3) they are easily transferable from the environment to the organisms in contact with them and (4) their reaction with other substances results in the increased levels of toxicity and bioavailability (Souza et al., 2020). According to

the previously mentioned Ordinance on the Protection of Agricultural Land from Contamination (*Official Gazette*, 2010), the heavy metals regarded as contaminants that should be monitored are cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn). In addition to these heavy metals, cobalt (Co), arsenic (As), and antimony (Sb) were included in the European Commission's LUCAS project for a study of the topsoil layer (Tóth et al., 2016). According to Zwolak et al. (2019), the heavy metals toxicity to the human health and the environment increases according to the relations: $Hg > Cu > Zn > Ni > Pb > Cd > Cr$. An agricultural land contamination by heavy metals is caused by a direct entry or by a gradual mobility of heavy metals and their accumulation in the land. The maximum threshold values of heavy metals in an agricultural land for the sake of a contamination declaration in the Republic of Croatia are figured in Table 1 (*Official Gazette*, 2010). The threshold values of a heavy metal soil content are defined according to the soil texture, soil pH, and the humus content. A recent study in central Croatia supported this method, as soil texture, soil pH, and soil organic matter values resulted in a strong correlation with the heavy metal soil contents (Ružičić et al., 2019). A soil texture exerts the greatest impact on the prescribed threshold values and is divided into three main categories: sandy, silty-loamy, and clay soils. The impact of soil texture on a heavy metal contamination is due to a stronger retention of heavy metals in the clay soils compared to the sandy ones, which are more porous due to the larger particle dimensions (Ke-Lin et al., 2006). The soil pH value determines the threshold values in the acidic soils, where the pH value of 6.0 is the reference value for Cd, Ni, and Zn, while the same applies to the pH value of 5.0 for Cr and Pb. If the pH values in the clay soils are lower than the reference values, the stricter threshold values are applied to the silty-loamy soils. The acidic silty-loamy soils are evaluated using the same process, to which the threshold values for the sandy soils apply (*Official Gazette*, 2010). The research conducted by Zeng et al. (2011) confirmed the dependence of a total heavy metal soil content on the pH value and the soil organic matter. Furthermore, Zhao et al. (2010) proved that the soilborne pH has a significant impact on the bioavailability of heavy metals in the soil due to the effects of solubility and the heavy metals' chemical speciation. The threshold value of soil humus content for Cu and Hg amounts to 3.0%, meaning that the lower values for agrillaceous soils indicate a necessity to use the maximum permitted values for the silty-loamy soils. The lower values for silty-loamy soils require the usage of the maximum permitted values for the sandy soils, accordingly (*Official Gazette*, 2010). A high soil humus content is associated with the immobilization of heavy metals in the soil (Chaturvedi et al., 2006).

The level of agricultural land contamination by heavy metals is classified into five categories and is determined by the ratio of a total heavy metal soil content, with the maximum threshold value expressed in percentages (Table 2).

Table 1. The maximum permitted heavy metal contents in the agricultural land in mg kg⁻¹ (Official Gazette, 2010)Tablica 1. Maksimalno dopuštene količine teških metala na poljoprivrednome zemljištu u mg kg⁻¹ (Official Gazette, 2010.)

Soil texture <i>Tekstura tla</i>	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Sandy soil	0.0 – 0.5	0 – 40	0 – 60	0.0 – 0.5	0 – 30	0 – 50	0 – 60
Silty-loamy soil	0.5 – 1.0	40 – 80	60 – 90	0.5 – 1.0	30 – 50	50 – 100	60 – 150
Clay soil	1.0 – 2.0	80 – 120	90 – 120	1.0 – 1.5	50 – 75	100 – 150	150 – 200

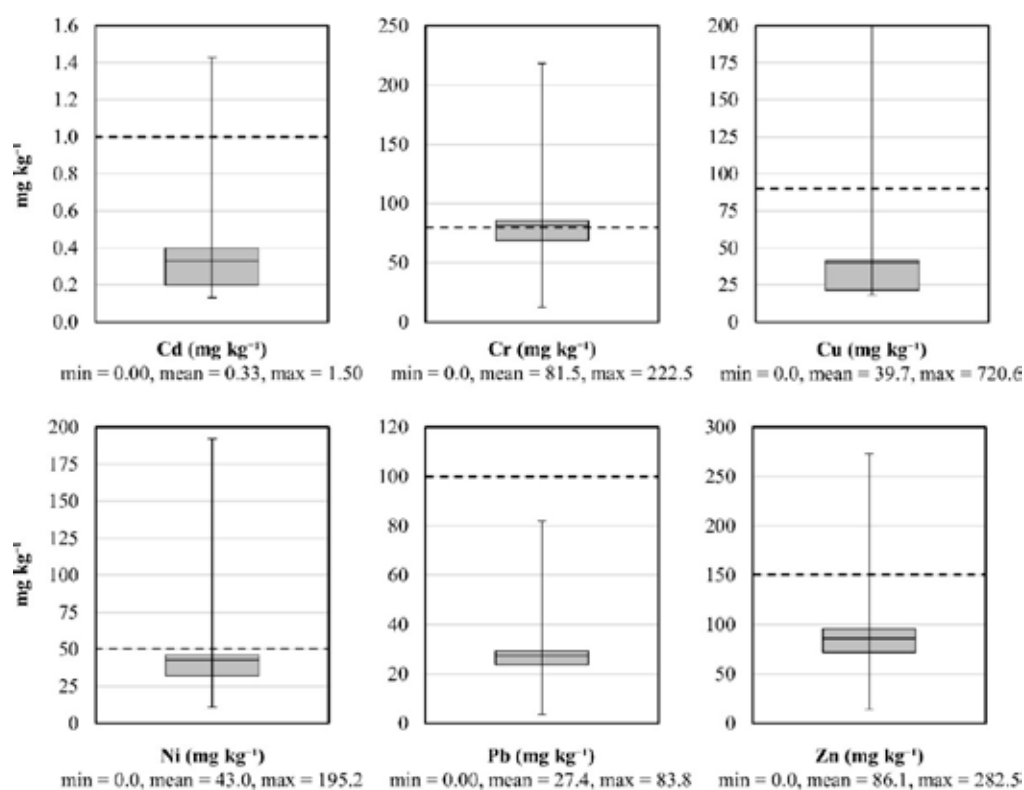
Table 2. Categories of land contamination by heavy metals (Official Gazette, 2010)

Tablica 2. Kategorije onečišćenja zemljišta teškim metalima (Official Gazette, 2010.)

Land-based heavy metal contamination levels <i>Stupanj onečišćenja zemljišta teškim metalima</i>	Contamination level percentage <i>Postotak stupnja onečišćenja</i>
Clean, uncontaminated land	< 25%
Land with an increased contamination	25 – 50%
Land with a high contamination	50 – 100%
Contaminated land	100 – 200%
Polluted land	200% >

The present levels of an agricultural land contamination caused by the heavy metals were analyzed according to 205 soil samples collected in 2016 in an agricultural land by the Croatian Ministry of Environmental Protection and Energy (Fig. 1). These soil samples contain the total heavy metal soil contents at a 0–30 cm soil depth for Cd, Cr, Cu, Ni, Pb and Zn, with the absence of Hg data. The boxplots of the heavy metal soil contents indicate the first quartile, the mean, and the third quartile values, with the black

lines designating the minimum and maximum values. The dashed lines indicate the maximum permitted heavy metal soil contents for the silty-loamy soils, as the dominant soil texture category in the majority of Croatia (Radočaj et al., 2020). It was observed that all the heavy metals in Croatia, except Pb, cause an agricultural land contamination to some degree. The Cr mean values at the country level exceed the maximum permitted soil content by 1.5 mg kg⁻¹, followed by Ni, Zn, and Cu as frequent contaminants.

**Figure 1. Heavy metal soil contents in Croatia's agricultural land, obtained by a national-level soil sampling**

Slika 1. Sadržaj teških metala na poljoprivrednome zemljištu Hrvatske iz uzorkovanja tla na državnoj razini

The prediction of heavy metals' spatial distribution in an agricultural land is a necessity for the knowledge of contamination levels caused by heavy metals, as well as the determination of strategies for soil remediation (Sollitto et al., 2010). Within the geographic information system (GIS) environment, it is possible to accurately predict the soilborne and topographic parameters (Šiljeg et al., 2020). The spatial interpolation process allows the determination of a continuous heavy metal distribution over the entire observed area (Sollitto et al., 2010). The collection of discrete soil sampling points necessitate an extensive field and laboratory work but also allow a limited representation of the heavy metal distribution in an agricultural land. These facts cause the spatial interpolation methods necessary for the monitoring of soil contamination caused by heavy metals in larger areas.

A spatial interpolation of heavy metal soil contents for the prediction of soil contamination levels in Croatia was performed by the Inverse Distance Weighting (IDW) interpolation method, which enables a high prediction accuracy of soil parameters in case of the sparse soil samples and the presence of extreme input values (Radočaj et al., 2020) (Fig. 2). Spatial interpolation was performed using a full dataset of 725 soil samples containing the total heavy metal soil contents at a 0–30 cm soil depth received from the Croatian Ministry of Environment Protection and Energy, with a spatial resolution amounting to 500 m. The agricultural areas were separated from the interpolation results using a generalized land cover class of agricultural areas from Corine Land Cover 2018 data.

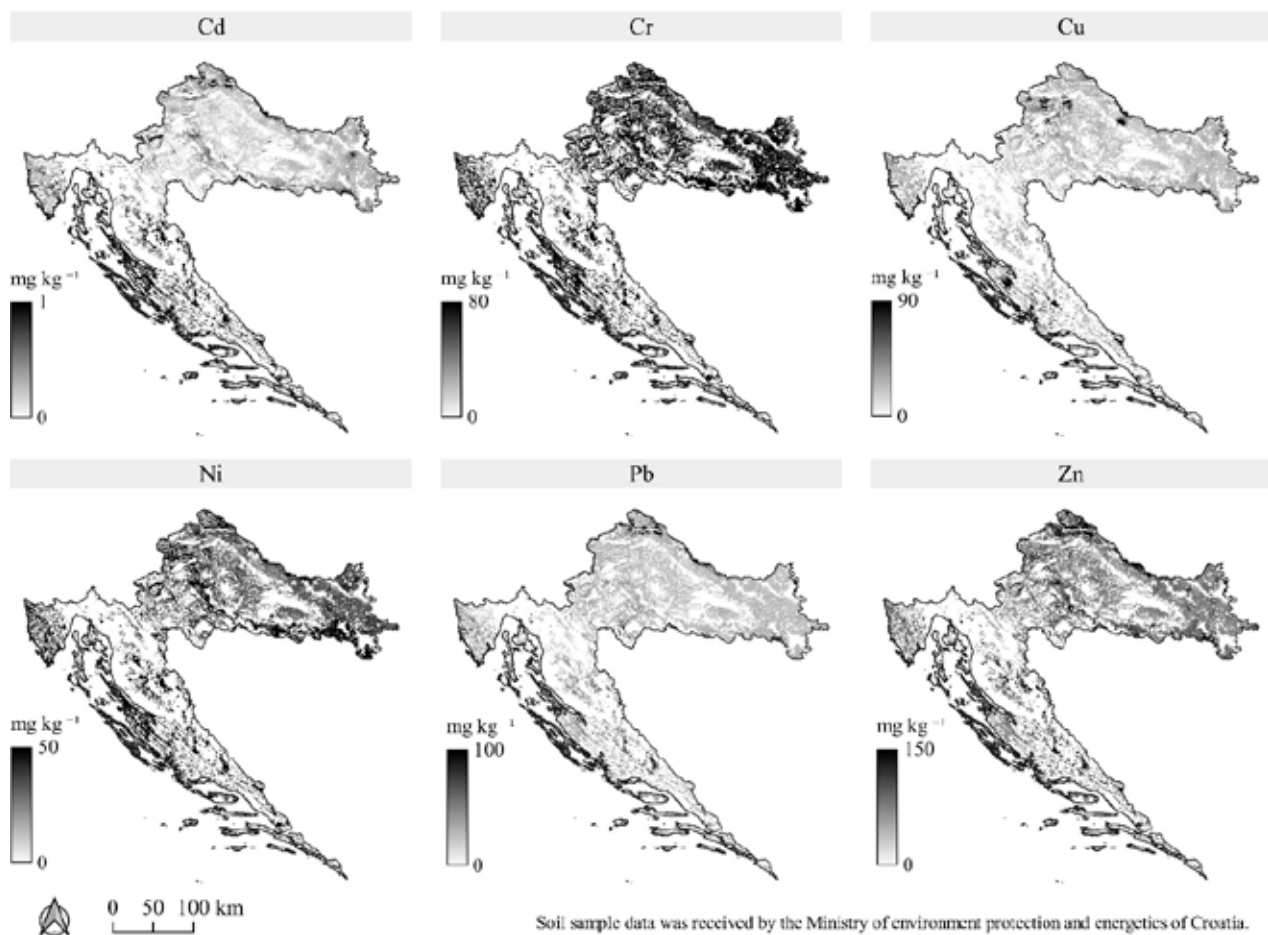


Figure 2. Spatial interpolation results pertaining to a heavy metal soil content distribution in Croatia's agricultural land
 Slika 2. Rezultat prostorne interpolacije sadržaja teških metala na poljoprivrednome zemljištu Hrvatske

The interpolated data were visualized according to the permitted heavy metal soil contents for the silty-loamy soils, defined by the Ordinance on the Protection of Agricultural Land from Contamination, with the dark area designating a land contaminated above these limits. The mean Cd values at the country level pertaining to the previous analysis did not indicate a high agricul-

tural land contamination, but the Mediterranean part of Croatia demonstrated a contamination above the maximum levels subsequent to a spatial interpolation. This case indicates the importance of spatial interpolation for the monitoring of soil contamination caused by heavy metals. The Cr soil content exceeded the levels of soil contamination and pollution in the majority

of Croatia's territory, while the only uncontaminated areas were detected in the central and far eastern parts of the country. A contamination caused by Cu and Pb was observed in the vicinity of the larger cities of industrial facilities, while Ni and Zn showed a high variability, except for the mountainous parts of Croatia.

Tiller (1989) divided the anthropogenic sources of heavy metal contamination into the deliberate and accidental ones (Table 3). The deliberate contamination sources are continuously distributed, with no clear impact boundaries. The accidental contamination sources are defined as the point sources, with a permanent source of contamination. In both cases, the heavy metals are released into the environment both in elemental form and as a part of various organic and

inorganic compounds (Khalid et al., 2017). According to Wuana and Okieimen (2011), more than 10% of insecticides and fungicides intended for crop treatment are based on the chemical compounds containing Cu, Hg, Pb, or Zn. Hasan et al. (2020) detected the heavy metal soil contents above the maximum permissible values for all contaminating heavy metals in the Mediterranean region of Croatia, with one of the main causes of agricultural land contamination being a low-quality fertilizer. While the most common sources of Cd, Ni and Zn contamination of agricultural land are related to the pesticides and fertilizers, the high soil content of Cr in Croatia is likely associated with the non-agricultural sources.

Table 3. Possible heavy metal contamination sources in an agricultural land (Alluri et al., 2007; Koul and Taak, 2018)

Tablica 3. Mogući izvori onečišćenja poljoprivrednoga zemljišta teškim metalima (Alluri i sur., 2007.; Koul i Taak, 2018.)

Heavy metal / Teški metal	Possible contamination sources / Mogući izvori onečišćenja
Cd	pesticides, fertilizers, welding, contaminated sewage sludge
Cr	wood industry, stainless steel industry
Cu	pesticides, fertilizers, paints, pottery industry
Hg	pesticides, improper disposal of batteries, paper industry
Ni	pesticides (herbicides), fertilizers, ceramics and stainless steel industry
Pb	pesticides, fertilizers, exhaust gases, mining, artificial paints
Zn	pesticides, fertilizers, municipal waste, oil refineries

REMEDICATION TECHNOLOGIES

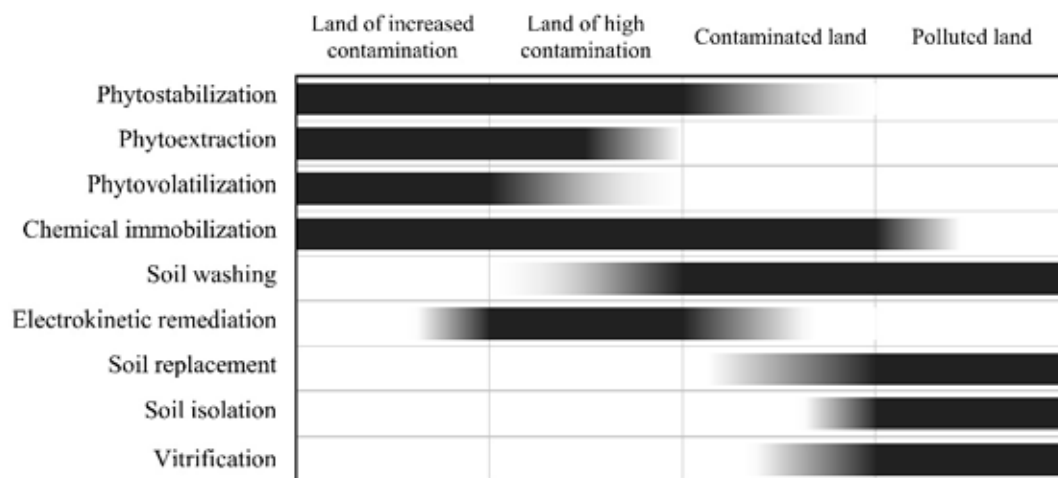
Some of the most commonly used biological, chemical, and physical remediation technologies are listed in Table 4 and described below. The selection of an appropriate soil remediation technology is primarily conditioned by the chemical and physical properties of heavy metals causing soil contamination (Wuana and Okieimen, 2011). The secondary factors that determine a selection of optimal remediation technology are cost, contamination-related spatial distribution, remediation durability and substance availability (Lim et al., 2014). Another commonly used remediation technology classification is the *in-situ* and the *ex-situ* technologies. The term *in-situ* refers to the technologies that are intended to treat the soil at the site of contamination. The effect of the *in-situ* remediation technologies depends on several agricultural land factors, such as the soil pH, moisture, drainage and distance from the sources of electricity (Koul and Taak, 2008). Although most remediation

technologies can be applied *in-situ* and *ex-situ*, *in-situ* is a more common choice on soils with the low or moderate contamination levels due to a lower implementation cost. The *ex-situ* remediation technologies include the removal of contaminated soil from its original site and the treatment in a laboratory or plant for the sake of a soil remediation. These technologies are applied to the severe cases of environmental contamination, whereby a soil removal is necessary to avoid a significant environmental risk (Martin and Ruby, 2004). The advantage of this approach is its time-efficiency of remediation, but it is often accompanied by a relatively high cost and a large amount of toxic waste that requires disposal at special landfills. Figure 3 displays the economic viability of the individual remediation technologies according to an agricultural land's contamination level. Although this assessment is based on the economic viability and is applicable in most cases, each case of soil contamination should be managed according to its specific properties.

Table 4. The most commonly applied remediation technologies, their advantages, and areas of application (Khalid et al., 2017; Song et al., 2017; Souza et al., 2020)

Tablica 4. Najčešće korištene remedijacijske tehnologije, njihove prednosti i područja primjene (Khalid i sur., 2017.; Song i sur., 2017.; Souza i sur., 2020.)

	Remediation technology / Remedijacijska tehnologija	Dominant areas of application and advantages <i>Dominantno područje primjene i prednosti</i>	
Biological group <i>Biološka skupina</i>	Phytostabilization / <i>Fitostabilizacija</i>	<i>In-situ</i> , cost-effectiveness, simplicity and accessibility, mildly and moderately contaminated agricultural land, remediation of large areas	Applicable for severely contaminated land
	Phytoextraction / <i>Fitoekstrakcija</i>		Possibility of permanent removal of heavy metals
	Phytovolatilization / <i>Fitovolatilizacija</i>		Low level of maintenance after establishment
Chemical group <i>Kemijska skupina</i>	Chemical immobilization / <i>Kemijska imobilizacija</i>	<i>In-situ</i> , cost-effectiveness, simplicity and accessibility, a high efficiency for cadmium remediation	
	Soil washing / <i>Ispiranje tla</i>	<i>Ex-situ</i> , very high remediation efficiency of numerous toxic heavy metal compounds	
	Electrokinetic remediation / <i>Elektrokinetička remedijacija</i>	<i>In-situ</i> , high remediation efficiency on agricultural land with a high content of finer particles and a lower soil pH	
Physical group <i>Fizikalna skupina</i>	Soil replacement / <i>Zamjena tla</i>	<i>In-situ</i> , simplicity and accessibility, severely contaminated agricultural land	
	Soil isolation / <i>Izolacija tla</i>	<i>In-situ</i> , limitation of heavy metal compounds mobility in soil, compatibility with the chemical or biological technologies	
	Vitrification / <i>Vitrifikacija</i>	<i>In-situ</i> , ease of application, a high efficiency for the remediation of mercury compounds	

**Figure 3. Economic feasibility of remediation technologies regarding a soil contamination level**

Slika 3. Ekonomska isplativost primjene remedijacijskih tehnologija s obzirom na razinu onečišćenja tla

Biological remediation technologies

Biological remediation technologies comprise the *in-situ* technologies based on the application of plants (phytoremediation) and microorganisms (bioremediation) for the decomposition of organic compounds that cause contamination or immobilization of the inorganic heavy metal compounds (Helmisaari et al., 2007). In recent studies, the bioremediation technologies, based on the application of microorganisms, demonstrated a success with regard to the remediation contaminated by heavy metals, but is still widely regarded as insufficiently researched for the sake of a reliable application in the field (Fernández et al. 2018). Instead of removing the heavy metal compounds from a contaminated soil, these compounds are often transformed into the less harmful organic compounds or oxidation states

using phytoremediation (Garbisu and Alcorta, 2001). The resulting compounds are usually less toxic, which indirectly affects their removal from the environment, individually or in combination with other remediation technologies. Laghlimi et al. (2015) noted the advantages of phytoremediation over conventional remediation technologies concerning a lower implementation cost and a long-term sustainability, while preventing the generation of large amounts of waste that has a negative impact on the environment. Phytoremediation can be applied to the soils with the mild and moderate contamination levels as a stand-alone remediation technology. In case of the severely contaminated soils, phytoremediation is applied in combination with the chemical or physical technologies. The advantages of phytoremediation are cost-efficiency and accessibil-

ity, as it requires the same technological conditions as a crop production (Wuana and Okieimen, 2011). For the application of phytoremediation, the optimal agroecological conditions are required for the cultivation of appropriate plant species for soil remediation, conditioned primarily by the climate, pedological, and topographic factors. The property of heavy metals accumulation in plants is most important for the selection of an optimal phytoremediation medium. The best choice are the plants that tolerate up to 1000 times higher concentration of heavy metals compared to other plants, known as hyperaccumulators (Suman et al., 2018). The phenological cycles of these plants generally last for several months and negatively affect the time efficiency of soil remediation, which is one of the greatest shortcomings of this technology (Ahmadpour et al., 2012). The hyperaccumulators with the shallow roots restrict the remediation extent to the topsoil layer, which makes the tree species more suitable for

the remediation of heavy metals in the deeper soil layers due to the deeper root systems. Phytoremediation comprises several remediation strategies, three of which have received the most attention in the literature: phytostabilization, phytoextraction, and phytovolatilization. The aforementioned strategies differ from each other primarily in the way of heavy metal compound accumulation. Phytostabilization immobilizes the heavy metal compounds in the root or in the rhizosphere, phytoextraction accumulates them in the root or in a leaf biomass, while in phytovolatilization the toxic compounds pass through the plant and are released into the atmosphere by a transpiration process (Fig. 4). These technologies are commonly applied interchangeably, alongside with other phytoremediation technologies, such as phytodegradation, rhizodegradation, and rhizofiltration, which are also especially effective in the groundwater remediation (Environmental Protection Agency, 2000).

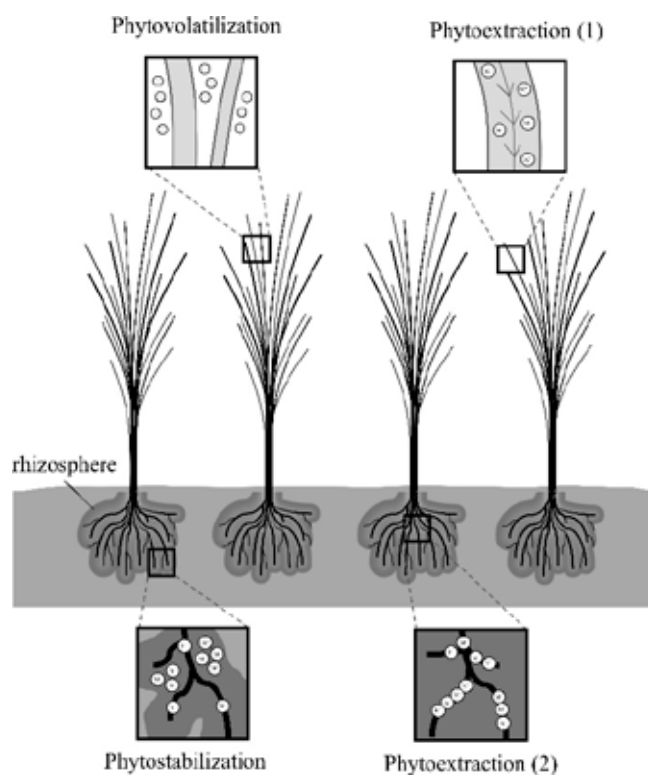


Figure 4. Heavy metal accumulation types with the usage of different phytoremediation strategies

Slika 4. Način akumulacije teških metala korištenjem različitih strategija fitoremedijacije

Phytostabilization is based on the immobilization of inorganic heavy metal compounds that cause contamination of an agricultural land through their accumulation in the root or in the rhizosphere (Bolan et al., 2011). Unlike phytovolatilization and phytoextraction, phytostabilization is also applicable to a severely contaminated soil due to the possibility of binding heavy metal compounds in the root or in the rhizosphere (Shackira and Puthur, 2019). Immobilization causes a reduced mobility of these compounds in the environment through the groundwater or dust. The conditions

for a phytostabilization plant selection are a high heavy metal tolerance and a possibility of their bioaccumulation, a large amount of biomass, and an extensively developed root system (Table 5). Phytostabilization also positively affects the fertility of a contaminated agricultural land. Since the contaminants remain in the soil during phytostabilization, this technology merely reduces their mobility in the soil and does not permanently eliminate the source of contamination, which is one of the main disadvantages of this approach.

Table 5. The select plants used in the phytostabilization of an agricultural land (Shackira and Puthur, 2019; Galić et al. 2019)

Tablica 5. Odabrane biljke za fitostabilizaciju poljoprivrednoga zemljišta (Shackira i Puthur, 2019.; Galić i sur. 2019.)

Plant name / Naziv biljke	Accumulated heavy metals / Akumulirani teški metali
Perennial ryegrass (<i>Lolium perenne</i> L.)	Cu
Ricinus (<i>Ricinus communis</i> L.)	Cd
Hemp (<i>Cannabis sativa</i> L.)	Cd, Cr
<i>Lupinus uncinatus</i> L.	Cd, Zn
Cowpea (<i>Vigna unguiculata</i> L.)	Cd

Phytoextraction is the process of heavy metals accumulation in the plant parts that can be harvested and therefore permanently removed from the soil (Suman et al., 2018). The plant parts that accumulate the heavy metals in a phytoextraction process are primarily the root system and the leaf biomass. A vegetation used in phytoextraction must meet two primary conditions: a large amount of biomass produced and a high efficiency of heavy metal accumulation in the plant parts that can be easily harvested (Table 6). The harvested plant parts subsequent to the phytoextraction can be composted or burned in a safe way (Garbisu and Alcorta, 2001). A contamination-related phytoextraction

caused by the presence of heavy metals in a deeper soil layer is also possible using the deciduous trees, since on this occasion the accumulated heavy metals mostly accumulate in the leaves (Unterbrunner et al., 2007). The tree species are particularly beneficial in phytoextraction due to a large biomass, as well as due to the deep and well-developed root systems, which allow an effective remediation of heavy metals in the deeper soil layers (Di Lonardo et al., 2010). In addition to the agricultural land remediation, agroforestry enables the exploitation of timber and is one of the possible strategies for a sustainable agricultural production in the future (Volk et al., 2006).

Table 6. The select plants used in the phytoextraction of an agricultural land (Unterbrunner et al., 2007; Rafati et al., 2011)

Tablica 6. Odabrane biljke za fitoekstrakciju poljoprivrednoga zemljišta land (Unterbrunner i sur., 2007.; Rafati i sur., 2011.)

Plant name / Naziv biljke	Accumulated heavy metals / Akumulirani teški metali
Crimson-Spot Rockrose (<i>Cistus ladanifer</i> L.)	Cd, Co, Cr, Ni, Zn
Brown mustard (<i>Brassica juncea</i> L.)	Pb, Zn
White poplar (<i>Populus alba</i> L.)	Cd, Cr, Ni
Birch (<i>Betula</i> L.)	Zn
Willow (<i>Salix</i> L.)	Cd, Zn

Phytovolatilization is based on the accumulation of heavy metal compounds in different parts of the plant and their transpiration or release into the atmosphere in the same or in an altered state (Ahmadpour et al., 2012). The heavy metal compounds released in that way are diluted and photochemically decomposed in the atmosphere, transferring a contamination to the environment to a much lesser extent. The transpiration process is enabled in a direct way by a transpiration of the accumulated compounds through the leaves and stems immediately into the atmosphere, or in an indirect way, whereby a transpiration occurs from the roots through the soil (Limmer and Burken, 2016). The advantage of phytovolatilization lies in a low requirement for the maintenance of a remediation process after implementation, since a phytovolatilization process is conditioned exclusively by the natural functions of vegetation. This process was proven effective for the remediation of inorganic compounds of

Hg, As, and selenium (Se) from the contaminated soils (Limmer and Burken, 2016). The main disadvantage of this approach is a still insufficiently researched contamination level transferred to the atmosphere by transpiration, especially in the urban areas. Kumar et al. (2017) cite a variable phytovolatilization remediation efficiency according to annual climate factors.

Chemical remediation technologies

Chemical immobilization is based on an *in-situ* application of immobilizing organic and inorganic substances to reduce the mobility of heavy metals in the soil (Hashimoto et al., 2009). Immobilizing substances cause the transformation of heavy metals into the chemically more stable states, which reduces their toxicity (Nejad et al., 2018). The absorption of heavy metals by agricultural crops and their entry into the food chain is also reduced (Zeng et al., 2020). Chemical

immobilization is generally one of the most economical remediation technologies and allows a high remediation efficiency for the Cd, Cu, Pb and Zn compounds (Zhou

et al., 2017). Some organic and inorganic substances used in immobilization, which are also widely available in Croatia, are shown in Table 7.

Table 7. The select organic and inorganic materials used in chemical immobilization (Guo et al., 2006)

Tablica 7. Odabrane organske i anorganske tvari korištene pri kemijskoj imobilizaciji (Guo i sur., 2006.)

Substance type / Vrsta tvari	Material / Materijal	Immobilized heavy metals / Imobilizirani teški metali
Organic	Sewage sludge	Cd
	Poultry manure	Cd, Cu, Pb, Zn
	Cattle manure	Cd
	Straw	Cd, Cr, Pb
Inorganic	Lime	Cd, Cu, Ni, Pb, Zn
	Cement	Cr, Cu, Pb, Zn
	Flyash	Cd, Cr, Cu, Pb, Zn

A soil leaching technology represents a combination of chemical and physical processes aimed at an *ex-situ* removal of heavy metals using various solvents and other liquids (Funari et al., 2017). Chemical soil leaching is based on a selective transition of heavy metals from the soil particles to the leaching solution. Due to a property of most heavy metals, which are insoluble in water, the chemicals are commonly added to the water to increase the leaching efficiency. The extracted contaminants are disposed at the specific landfills and can still be treated using the chemical or biological agents (Dermont et al., 2008). A rehabilitated soil subsequent to the leaching usually contains 50-80% of the original contaminated soil mass, which depends on the level of soil contamination and the transporting cost of the waste generated in the landfill. A chemical soil leaching technology has enabled a very high remediation efficiency of a wide range of heavy metal compounds, including plutonium from a radioactive waste (Xu et al., 2016). Since soil leaching is cost-efficient only in smaller areas, this technology is primarily intended for a severely contaminated agricultural land.

An electrokinetic remediation is based on the application of direct electric current on a contaminated agricultural land, whereby the organic and inorganic toxic heavy metal compounds are extracted from the soil by a combination of electroosmosis and electromigration procedures (Yeung and Gu, 2011). The method of electrokinetic remediation is most effective in the soils with a high proportion of finer soil particles in the agrillaceous and silty soils (Khalid et al., 2017). The implementation of electrokinetic remediation is performed by the electrodes, which affect the pH value of an agricultural land and immobilize the toxic heavy metal compounds (Koul and Taak, 2018) by generating the H⁺ and the OH⁻ ions at the anode and cathode, respectively. The particles containing the toxic heavy metal compounds in the soil gradually move toward the electrodes of an opposite charge in an electric field. The low pH value of

the soil allows for a greater heavy metal solubility, which requires the application of electrokinetic remediation (Gill et al., 2014). Due to the high complexity of electrochemical processes in the soil, the need for an optimal soil pH, and electricity source, this technology does not independently enable an efficient soil remediation (Li et al., 2016).

Physical remediation technologies

The remediation of agricultural land by soil replacement is based on a simple principle of full or partial *in-situ* replacement of a soil contaminated with heavy metals by a clean soil (Khalid et al., 2017). A soil replacement dilutes the contaminating heavy metal compounds, thus improving a soil functionality and fertility. Originally contaminated soil removed from an agricultural land is treated with some of the *ex-situ* remediation technologies or disposed of at special landfills (Koul and Taak, 2018). Although the implementation of this approach is technologically undemanding, the costs of labor and soil transport make this technology economical only in case of a severely contaminated agricultural land in a smaller area.

A soil isolation differs from other remediation technologies, since it is not aimed at removing or immobilizing the toxic heavy metal compounds in the soil but at limiting their mobility in a defined spatial extent (Zhu et al., 2012). This technology is not intended for the individual applications on a contaminated agricultural land but as a contamination emergency activity or as a supplement to other remediation technologies (Khalid et al., 2017). Various underground barriers are commonly used for soil isolation, which prevents the transition of heavy metals to the groundwater and reduces their mobility in the environment. Due to the cost of labor and the establishment of underground barriers, this technology is economically justified only for a severely contaminated agricultural land, combined with the chemical or biological remediation technologies.

A vitrification technology is implemented by treating a contaminated soil with high temperatures, thus reducing the mobility of heavy metal compounds in the soil (Liu et al., 2018). This technology is flexible, since it supports an *in-situ* or an *ex-situ* treatment of both the organic and inorganic heavy metal compounds. An *in-situ* vitrification is a more commonly used approach due to financial cost-effectiveness and is based on the application of electric current to a contaminated soil by a regular grid arrangement of electrodes (Khalid et al., 2017). The temperatures during vitrification generally reach from 1050 to 1850°C, which is sufficient for the immobilization of various compounds containing Cu, Ni, Pb and Zn. Due to a low Hg melting point, this method is very effective in remediating an agricultural land contaminated with the Hg compounds, whereby their evaporation or decomposition occurs (Wuana and Okieimen, 2011). The limitations of a vitrification technology are the high implementation costs and electricity, as well as a requirement for the soils having a high moisture content and a low pH value.

THE POSSIBILITIES TO APPLY THE REMEDIATION TECHNOLOGIES IN CROATIA AND A CONCLUSION

A remediation technology analysis pertaining to an agricultural land contaminated by heavy metals identified the possibilities to apply the biological, chemical, and physical remediation technologies. The present contamination of agricultural lands by heavy metals above the maximum prescribed limits in Croatia has been detected for Cr, Ni, Zn, Cd and Cu using spatial interpolation. These observations indicate that the current soil remediation strategies should be reconsidered, and the prevention measures regarding the heavy metal input, predominantly via pesticides and fertilizers, should be stricter. The basic criteria for the recommendation of remediation technologies in Croatia were the contamination level of an agricultural land caused by a particular heavy metal and an economic viability. A necessary resource availability and a low human impact on the environment during remediation are the basic factors of a high phytoremediation potential for the sake of a wide implementation in Croatia, especially for the sake of a remediation of soils contaminated with Cd. The recent increase of hemp cultivation in Croatia could also bear future importance for the phytostabilization of soil Cd and Cr, being successfully applied to both the acidic and alkaline soils in Croatia (Galić et al., 2019). A phytostabilization using hemp and a chemical immobilization using straw are currently some of the most viable remediation strategies for a prevalent problem of Cr soil contamination in Croatia. A Zn soil contamination can be effectively treated by phytoextraction using the common tree species in Croatia, birch and willow, as well as by using various inorganic substances in chemical immobilization. The remediation of agricultural land contaminated with Ni offers a limited choice of strate-

gies in Croatia, so more emphasis should be put on the prevention of their input in the environment, most notably through the application of herbicides. For the more severely contaminated soils, the chemical and physical methods are the optimal alternatives, since phytoremediation can treat a mild or moderate soil contamination. The effective applicability of chemical and physical remediation technologies is limited concerning a severely contaminated soil, which includes a very small share of agricultural land, as contamination sources in these cases are the factories and unregulated landfills. A chemical immobilization is an exception in some cases due to the availability of remediation substances traditionally used in Croatia, such as the manure for fertilization and the straw and lime for various applications on farms. Raising an awareness pertaining to the heavy metal toxicity in agricultural production and the availability of resources for an effective remediation creates the foundations for an increased application of remediation technologies in Croatia.

ACKNOWLEDGEMENTS

This work was supported by the Faculty of Agrobiotechnical Sciences Osijek as a part of the scientific project 'AgroGIT – technical and technological crop production systems, GIS and environment protection'.

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REMEDIJACIJA POLJOPRIVREDNOGA ZEMLJIŠTA ONEČIŠĆENOG TEŠKIM METALIMA

SAŽETAK

Prisutnost teških metala na poljoprivrednome zemljištu primarni je uzrok toksičnosti prehrambenih proizvoda biljnoga i životinjskog podrijetla povezanih s onečišćenim poljoprivrednim zemljištem. Antropogeni izvori onečišćenja, posebno primjena umjetnih gnojiva i pesticida u ratarstvu, primarni su izvor onečišćenja poljoprivrednoga zemljišta teškim metalima. Teški metali čije je praćenje (monitoring) propisano važećom zakonskom regulativom Republike Hrvatske uključuju kadmij (Cd), krom (Cr), bakar (Cu), živu (Hg), nikal (Ni), olovo (Pb) i cink (Zn). Cilj rada bio je dati pregled teških metala koji uzrokuju onečišćenje poljoprivrednoga zemljišta, kao i remedijacijskih tehnologija koje se primjenjuju za smanjenje onečišćenja. U radu su razmatrane tri skupine remedijacijskih tehnologija, biološke, kemijske i fizikalne, i to sa stajališta primjenjivosti, učinkovitosti i ekonomičnosti te sa stajališta društvene prihvatljivosti i dostupnosti u Hrvatskoj, kako bi se potaknula njihova šira implementacija. Biološke remedijacijske tehnologije, poglavito fitoremedijacija, najbolje su zadovoljile postavljene kriterije, što ih trenutačno čini najprimjenjivijima za nisko i umjereno onečišćena poljoprivredna zemljišta. Kemijske i fizikalne remedijacijske tehnologije općenito su pogodnije za remedijaciju teže onečišćenoga poljoprivrednog zemljišta, primijenjene samostalno ili u kombinaciji s metodama fitoremedijacije zbog visokih troškova.

Ključne riječi: teški metali, onečišćenje tla, antropogeno onečišćenje, remedijacijske tehnologije, fitoremedijacija

(Received on September 23, 2020; accepted on October 30, 2020 – *Primljeno 23. rujna 2020.; prihvaćeno 30. listopada 2020.*)