Phytoremediation of Soils Contaminated with Heavy Metals in the Vicinity of the Smelter for Lead and Zinc in Veles

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Summary

Soil quality is one of the most important factors in sustaining the global biosphere, but it is subject of a series degradation processes or threats. Contamination of the soils with heavy metals is one of them.

The region around Veles is one of the typical examples of soil pollution and other environmental media by toxic metals, such as: lead, cadmium, zinc and others, as a result of emission of those elements from the lead and zinc smelters located in Veles.

The accumulation of heavy metals in the food chain, especially of lead (Pb) and cadmium (Cd) from soil through the consumption of vegetables, may affect the human and environmental health.

To find adequate measures to prevent present ecological problems, we have to use appropriate and successful actions. Phytoremediation is a relatively new emerging green technology that uses plants to extract heavy metals from contaminated soils. This paper presents a research in which four test plants (oilseed rape – *Brassica napus Oleifera* D.C., white clover - *Trifolium repens* L., alfalfa - *Medicago sativa* L., and corn – *Zea mays* L.) were cultivated in industrially polluted soils in order to find a suitable plant species that could be used for soil remediation in industrial regions.

The comparison between the examined crops during the three-year research period in relation to the heavy metal bioaccumulation coefficient indicated that for phytoremediation of soils with high Pb concentration the alfalfa can be recommended, for soils with high Cd concentration oilseed rape and white clover are preferable, and on soils with high Zn concentration alfalfa and white clover are superior.

Key words

phytoremediation, heavy metals, soil

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Introduction

All soil researchers emphasize that soil is a finite natural resource. Technically, the soil is a renewable natural resource, because its formation goes on perpetually. However, due to the fact that pedogenesis is a very slow process, the soil is non-renewable for all practical purposes, and therefore scientists classify the soil as a conditionally renewable resource (Varallyay, 2000; Montanarella, 2007; cf. Ličina et al., 2011). Soil formation and restoration on the geological substrate take thousands of years, whereas the processes of soil degradation and soil losses are sometimes much more rapid and might occur in a matter of seconds or minutes, such is the case with soil erosion or other kinds of natural or anthropogenic accidents.

The increased industrialization, mining, smelting, electroplating, agriculture and other anthropogenic activities have concentrated various heavy metals and their compounds into the soil- water environment. Contaminated soils pose a major and serious environmental and human health problem.

In the Republic of Macedonia, 16 sites with soil contamination have been identified, characterized as hotspots (Environmental statistic, 2007). The region around Veles is one of the typical examples where this has been proved. Toxic metals such us lead (Pb), cadmium (Cd), zinc (Zn) and other, contaminated the soils and other environmental media in the surrounding area of the smelter that operated in Veles during the period from 1971 to 2002. The pollution of the soil in the town of Veles and its environment significantly increased as a result of 30 years of production in the smelter plant. These polluted soils with heavy metals are still used for horticultural and thus potentially can be highly risky for food safety and security (Jordanovska and Stafilov, 1996; Stafilov and Jordanovska, 1997). The studies of this region show high contamination of topsoil especially with Cd, Pb and Zn, as a result of pollution from the smelter plant (Stafilov et al., 2010).

In the materials prepared by the local government of municipality of Veles entitled as "Local Agenda 21 for municipality of Veles" many disturbing results about the soil contamination by heavy metals are presented. For instance, over the research area of 270 km^2, 468 soil samples were taken: 50.6% of them had > 90 mg kg^{-1} of Pb, 9% contained > 357 mg kg^{-1}, 16% contained 180 to 357 mg kg^{-1} and 25.6% had 90 to 180 mg kg^{-1}. High contamination of the soils by Pb and Zn provides favorable conditions for the uptake and accumulation of those elements into the aboveground parts of the cultures growing in Veles region (Mitkova et al., 2009; Prentović et al., 2009).

In the scientific literature one of the measures for revitalization of the contaminated soils with heavy metals is phytoremediation (Kumar et al., 1995; Salt et al., 1998; Petrović et al., 2002; Terry and Banuelos, 2000), which is the part of the bioremediation. It consists of growing different cultures that are able to do phyto-extraction of heavy metals from the soil solution and to do hyperaccumulation into the aboveground organs. Mowing the aboveground organs and removing them from the soil surface contributes to the soil gradual impoverishment with the present toxic metals. So, after a certain period of time, the contaminated soils will turn into an appropriate condition for production of healthy food. In addition, remediation plants must have mechanisms to detoxify and/or tolerate high metal concentrations accumulated in their shoots.

Material and methods

The experiment was set up on the productive areas of Public Communal Enterprise PCE "Derven in Veles", according to the randomized block system experimental design with four test plants (oilseed rape – *Brassica napus Oleifera* D.C., white clover - *Trifolium repens* L., alfalfa - *Medicago sativa* L., and corn – *Zea mays* L.) in four repetitions within a period of three years (2008-2010). The number of experimental zones was 16. Each of them was 3.0 m wide and 5.0 m long, thus covers an area of 15.0 m^2. The distance between the series was 1.0 m and between the treatments it was 0.5 m. The total area of experiment was 310.5 m^2. During the vegetation, the following parameters were observed: phenophases development of plant, plant height, number of plants per m^2 (vegetative composition) and the yield of green mass. Additionally, we took into account a higher planting density (20 kg ha^{-1} – oilseed rape, with between rows distance of 0.15 cm – 6 rows/zone; 10 kg ha^{-1} - white clover, with between rows distance of 0.15 cm - 20 rows/zone; 20 kg ha^{-1} - alfalfa, with between rows distance of 0.15 cm - 20 rows/zone and 30 kg ha^{-1} - corn with between rows distance of 0.55 x 0.25 cm, about 80.000 plants/ha) compared to standard agricultural practice. This was done in order to eliminate the chance of a smaller sprout due to the contaminated soil, as well as to secure a maximum biomass production.

Before the experiment, average soil samples were taken from 0-20 cm and 20-40 cm for determination of the total and soluble forms of heavy metals (lead, cadmium and zinc) in the soil. Preparation of soil samples was performed in accordance to the ISO 11464:2006 standard. Total soil concentrations of metals were extracted by the Aqua Regia (HCl-HNO_3, 3:1) method (ISO 11466:1995), their soluble forms were extracted by EDTA (Đamić et.al. 1996), whereas the plant material was degisted in a nitric acid (HNO_3) (Jones and Case, 1990) and in all extracts observed metals were detected by Atomic Absorption Spectrophotometry (AAS): Varian AA 220 with graphite furnace. The significant differences between the treatments were detected by means of the LSD test.

Results and discussion

There exist a number of conventional remediation technologies that are employed to remediate environmental contamination and soil contamination with heavy metals and other pollutants.

Concerning the decontamination of the contaminated soils it is practice to cultivate plants able for hyperaccumulation of the heavy metals that contaminate the soil. This measure in the literature is called phytoremediation (Sekulić et al., 2003). As a technology, it is considered to be sustainable, especially compared to conventional approaches to contaminated site remediation and/or management, since it is considered to be primarily solar powered (Bhandari et al., 2007). It is considered to be a "Green Revolution" in the field of innovative cleanup technologies (Hooda, 2007).

Table 1. Texture of the soil used for the experiment - fine soil separates in %

N	Coarse sand 0.2-2mm		Fine sand 0.02-0.2mm		Total sand 0.02-2mm		Silt 0.002-0.02mm		Clay <0.002mm		Silt+clay <0.02mm	
2	$\bar{x}$ %	SD	$\bar{x}$ %	SD	$\bar{x}$ %	SD	$\bar{x}$ %	SD	$\bar{x}$ %	SD	$\bar{x}$ %	SD
	23.10	2.69	55.10	3.68	78.20	6.36	11.60	1.84	10.20	4.53	21.80	6.36

$\bar{x}$ % - average; SD – standard deviation

Table 2. Chemical properties of tested soil used for experiment

N	Humus (%)		N (%)		pH in H_2O		pH in KCl		$CaCO_3$ (%)		P_2O_5 (mg/100g)		K_2O (mg/100g)	
2	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
	1.38	0.33	0.08	0.02	7.68	0.11	6.98	0.04	5.95	1.06	2.86	1.56	11.26	1.20

$\bar{x}$ - average; SD – standard deviation

Table 3. Content of heavy metals in the soil used for the experiment

N	Total (mg kg^{-1})						EDTA-extractable (mg kg^{-1})					
	Pb		Cd		Zn		Pb		Cd		Zn	
2	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
	176.80	1.18	5.58	0.21	330.34	12.03	81.60	10.47	3.46	0.25	64.27	2.04

$\bar{x}$ - average; SD – standard deviation

The design of a phytoremediation system varies according to the contaminants, the conditions at the site, the level of cleanup required, and the plants used. As previously noted, contaminants and site conditions are perhaps the most important factors in the design and success of a phytoremediation system. Phytoremediation is an agronomic process. It is highly dependent on climate and site-specific characteristics. Soil properties determine the ability of a plant species not only to become established in the soil, but also to maximize biomass and, therefore, removal of contaminants.

The experiment was made on the right side of the bank of the Vardar River, formed with the sedimentation of the suspended alluvium from the river water. The region of Veles lies in the central part of Macedonia and is under influence of the Eastern-continental and modified Mediterranean climate. This combined influence of the two climates results in the most arid conditions: average annual temperature of 13.3^{0}C, average annual rainfall of 460 mm with low De Martonne drought index 23 and Lang's rain factor is 40 (Mitkova et al., 2009; Filipovski et al., 1996).

The fixation/mobilisation potential of the soil with respect to heavy metals is dependent on the pH, organic matter and clay content of the soil. Table 1 and 2 show the mechanical composition and chemical properties of the soil.

In soil separates, the fine sand fraction (55.10%) dominates and together with the coarse sand fraction amount to 78.20%, the silt fraction is third (11.60%) and the clay (10.20%) is the last abundant fraction. The soils are characterized by favorable mechanical composition that was confirmed with the classification of the fluvisols in texture classes (fine sandy loam) according to Scheffer and Schachtschabel (Mitrikeski and Mitkova, 2006).

The results of the research of the chemical properties of the alluvial soil (Table 2) show that the examined soil had little (1.38%) humus contents, medium contents of carbonates (5.95%) (Penkov, 1996) and low alkaline (pH = 7.68) reaction.

The neutral and low alkaline reaction of the soil solution as well as the organic and mineral colloids, limit the heavy metal mobility, including their easily available forms.

In the Republic of Macedonia we still refer to the EU standards on maximally permitted concentration of heavy metals in the soil. Maximum Allowable Concentrations (MAC) of trace elements in agricultural soils from EU standards should not be more than: 100 ppm of Pb, 150-300 ppm of Zn and 1-3 ppm of Cd (Kabata-Pendias et al., 2000). For our country Filipovski (2003) suggests the following MAC: 100 ppm of Pb, 200 ppm of Zn and 3 ppm of Cd.

The results on the total contents of heavy metals in the soil have indicated that all three elements are present over the maximally permitted concentrations (Table 3), which means that the soils are not safe for healthy food production.

This level of soil contamination is suitable for implementation of the phytoremediation measure that is not very efficient when it comes to greater contents of heavy metals in the soil.

The results from the three-year research (2008-2010) are shown in Table 4 and 5.

According to Blaylock et al. (1997,, cf. in Hajiboland, 2005), the efficiency of phytoextraction for a given species is determined by two key factors: biomass production and the metal bioaccumulation factor. Bioaccumulation coefficient is a ratio between the concentration of the metal present in the plant tissue and the

Table 4. Biomass production, total heavy metals concentrations in shoot dry matter ,and the coefficient of bioaccumulation for the different plant species grown in polluted soil during three year period

Plant	Biomass yield (t ha^{-1})	$mg\ kg^{-1}$ in the dry plant material			Coefficient of bioaccumulation		
		Pb	Cd	Zn	Pb	Cd	Zn
lucerne/alfalfa	222.32a	18.43a	0.576b	105.26a	0.23	0.17	1.64
oilseed rape	192.24b	14.5c	1.29a	54.93b	0.18	0.37	0.85
white clover	83.90c	15.62bc	1.19a	102.27a	0.19	0.34	1.59
corn	79.79c	16.78b	0.702b	48.42b	0.21	0.20	0.75

Table 5. Average annual biomass production, heavy metals concetrations in shoot dry matter and the coefficient of bioaccumulation for the different plant species grown in polluted soil during three year period

Plant	Biomass yield (t ha^{-1})	$mg\ kg^{-1}$ in the dry plant material			Coefficient of bioaccumulation		
		Pb	Cd	Zn	Pb	Cd	Zn
lucerne/alfalfa	74.11a	6.14a	0.19b	35.09a	0.08	0.06	0.55
oilseed rape	64.08b	4.83c	0.43a	18.31b	0.06	0.12	0.28
white clover	27.96c	5.21bc	0.40a	34.09a	0.06	0.11	0.53
corn	26.59c	5.59b	0.23b	16.14b	0.07	0.07	0.25

*numbers in same column with same letter are not significantly different at level 0.05

starting concentration of the metal in the soil solution (Sekulić et al., 2003; Kumar et al., 1995).

The results showed that the highest total biomass yield for the three-year trial period was observed in alfalfa, and it was significantly higher than in all other three crops. Characterized by the highest biomass yield, alfalfa was superior in extracting Pb (18.43 mg kg^{-1}) from the soil, significantly higher quantity than all other crops, and Zn (105.26 mg kg^{-1}), of which extraction was the same as in the white clover (102.27 mg kg^{-1}). The highest quantity of Cd was extracted by oilseed rape (1.29 mg kg^{-1}), and it was not significantly different from white clover (1.19 mg kg^{-1}). The obtained values for the coefficient of accumulation (Table 4 and 5) only confirmed these observations. It can be concluded that not in every case the crops characterized with the highest biomass yield have the highest bioaccumulation of heavy metals. On opposite, the white clover, with an average yearly biomass yield of only 27.96 t ha^{-1}, didn't differ significantly considering the extraction of Cd and Zn from oilseed rape and alfalfa, which had significantly higher biomass yield than the white clover.

Conclusion

The results of the total contents of heavy metals in the soil have indicated that all three observed heavy metal elements were presented over the maximally permitted concentrations that means that the soils are not safe for healthy food production. This level of soil contamination is suitable for implementation of the phytoremediation measure that is not very efficient when it comes to greater contents of heavy metals in the soil.

The comparison between the examined crops during the three-year research period in relation to the heavy metal bioaccumulation coefficient indicated that for phytoremediation of soils with high Pb concentration the alfalfa can be recommended, for soils with high Cd concentration oilseed rape and white clover are preferable, and on soils with high Zn concentration alfalfa and white clover are superior.

This is the first scientific knowledge on the phytoremediation of soils with heavy metal contamination in Macedonia, and further research is needed in order to better exploit the possibilities for phytoremediation of the national soils.

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