

STUDY OF THE TRITICUM DURUM REHABILITATION CULTIVATED IN A HEAVY METAL CONTAMINATED SOIL BY USING ENVIRONMENTALLY FRIENDLY MATERIALS

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Abstract

The heavy metal contaminated soils is one of the most important problems in the field of rural development. Heavy metals can easily enter in the food chain. The transportation of heavy metals from soils to the upper part of the plants and then through the food to humans and animals can have negative effects in many living organisms. Durum wheat is one of the cereals which is cultivated in large areas all over the world. The aims of this work were (1) to study the accumulation of five heavy metals (Cu, Cr, Zn, Ni, Pb) in plants of durum wheat, (2) to reduce the availability of the pollutants to durum wheat plants by using three different mixture of manure and attapulgite (1:3, 1:1, 3:1) at three different levels (0%, 3% and 4% mix of manure - attapulgite / Kg soil) and (3) to evaluate the positive effectiveness of the different treatments. A pot greenhouse experiment was conducted in the University of Thessaly in Volos (Greece). For the pot experiment a heavy metal contaminated soil from an area that is near in the large motorways in Larissa region was collected. The agricultural soil and plant samples were analyzed for their "pseudo-total" heavy metals content by using the atomic absorption spectrophotometer. Furthermore, the Transfer Coefficient (Tc) was measured. According the results, the addition of mixture of manure and attapulgite reduces the uptake of metal pollutants in the soil. Furthermore, the results have shown that each treatment had a different effect on the reduction of heavy metals in the soil and in the transportation of heavy metals from the soil to upper part of the durum wheat plants.

Keywords: heavy metals, contamination, *Triticum durum*, attapulgite

1. INTRODUCTION

In recent years in most developing countries the rapid increase of the industrialization has caused significant problems in air, water and soil quality. Particularly, the existence of heavy metals (HMs) in agricultural regions, due to human activities, has caused adverse effects on plants, animals and on human health. Heavy metals can easily enter to the human food chain by direct consumption of plants and indirect via the animal consumption. These pollutants can be hazardous for all the living organisms when they are under the safety limits (Gupta *et al*, 2021; Gulten, 2011).

The most common heavy metals that exist in a contaminated soil are lead, chromium, copper, zinc, cadmium and nickel (Bhagat *et al.*, 2021).

The agricultural fields which is near in large motorways can be adversely affected by the heavy traffic and by the road dust which produced from the large amount of vehicles. The road dust releases pollutants, such as heavy metals, in the in the atmosphere (Duong and Lee, 2011).

Most of the plants that are used for the human food are able to adsorb the heavy metals from the soil and deposit them to the edible parts. One plant category that can be affected negatively from the heavy metals are cereals. Cereals are the most popular food all over the world. One of these is the wheat which plays an important role for the animal and human (Souahi *et al.*, 2021).

That's way the contamination of the agricultural lands by heavy metals is a current problem with great concern.

A lot of technologies have been used for the rehabilitation soils from heavy metals such as chemical precipitation, membrane processes, ion exchange, coagulation, and flotation ((Bhagat *et al.*, 2021). The last years, because the high cost of these methods, for the HMs removal has begun to be used materials that are environmental friendly. Materials like these are the use of organic and inorganic soil improvements such as manure and attapulgite. These adsorbents have proved to be more efficient and more economical (Krstic *et al.*, 2018).

Attapulgite is a magnesium aluminosilicate material with unique adsorptive properties. The uniqueness of attapulgite its the very large specific surface area and its porosity (Pyrgaki *et al.*, 2018).

It has been proved that the organic soil amendments besides the fact that can improve the crop production, the aeration and the water retention, they are able to have a positive effect on the intake of heavy metals by plants (Chen *et al.*, 2021)

The use of different adsorbents for the removal of heavy metals from soil and plants is a promising research field.

Thus, the objective of this thesis was to study if the different mixtures of manure and attapulgite at two different levels have the capacity to reduce the heavy metals concentration in a contaminated soil and also to study the possibility of a safe *Triticum durum* cultivation in contaminated soil using soil improvement.

2. MATERIALS AND METHODS

2.1. Materials

The contaminated soil that used for the pots experiment was collected from an area that in near in large motorways in Larissa region (CS). This soil was chosen among a lot of soil samples which were collected from the specific area.

The soil was air-dried at room temperature and sieved through a 2 mm. Then it was used to fill the pots (4 kg soil per pot).

Treatments which were included a mixture of manure and attapulgite (25% manure and 75% attapulgite, 50% manure and 50% attapulgite and 75% manure and 25% attapulgite) applied in the soil at three different levels (0%, 3% and 4% mixture of manure - attapulgite / Kg soil) and for the cultivation was used the crop *Triticum durum*. In each pot about 20 *Triticum durum* seeds was be sown. The treatments, are presented in the Table 1. For every treatment was used three replicates. In the greenhouse was put 21 pots. The soil moisture was be maintained at 65% of its water capacity. After approximately 120 days of growth, the plants were harvested with their root system and washed thoroughly with deionized water to remove surface dust and soil. The plant tissue samples were dried for at least 48 hours at 70 °C, weighted and ground to <2 mm. Total concentration of Pb, Ni, Cu, Cr and Zn in the plants were assessed. Also, soil samples from each pot was collected. The "pseudo" total concentration of metals in the soil, after plant cultivation and the incorporation of soil improvements was determined.

Table 1. Treatments of the pot experiment

Code	Treatment
CS.TD	4 kg contaminated soil with the highest heavy metals concentration plus <i>Triticum durum</i>
CS.M1.TD	4 kg contaminated soil with the highest heavy metals concentration plus mixture of 25% manure – 75% attapulgite (3% mixture / kg soil) plus <i>Triticum durum</i>
CS.M2.TD	4 kg contaminated soil with the highest heavy metals concentration plus mixture of 50% manure – 50% attapulgite (3% mixture / kg soil) plus <i>Triticum durum</i>

CS.M3.TD	4 kg contaminated soil with the highest heavy metals concentration plus mixture of 75% manure – 25% attapulgate (3% mixture / kg soil) plus <i>Triticum durum</i>
CS.M4.TD	4 kg contaminated soil with the highest heavy metals concentration plus mixture of 25% manure – 75% attapulgate (4% mixture / kg soil) plus <i>Triticum durum</i>
CS.M5.TD	4 kg contaminated soil with the highest heavy metals concentration plus mixture of 50% manure – 50% attapulgate (4% mixture / kg soil) plus <i>Triticum durum</i>
CS.M6.TD	4 kg contaminated soil with the highest heavy metals concentration plus mixture of 75% manure – 25% attapulgate (4% mixture / kg soil) plus <i>Triticum durum</i>

2.2. Methods

The below physicochemical properties were analyzed in soil: pH (1:2.5 H₂O), CaCO₃ (Bernard densitometer), electrical conductivity (1:1 H₂O), particle size distribution (Bouyoucos hydrometer), and organic matter (Walkley – Black wet oxidation).

Total concentration of Pb, Ni, Cu, Cr and Zn in the plants were measured by using the Dry Ashing Procedure (Jones and Case, 1990).

Also, the soil samples were analyzed for their “pseudo-total” heavy metals content (Cr, Cu, Cd, Zn, Pb, Ni) by using *aqua regia* method (digestion at 140 °C for 5 hours with 3:1 concentrated HCl: HNO₃) (ISO/DIS 11466, 1994).

The total concentration of the heavy metals in plants and the concentration of pseudo - total heavy metals in soil samples were measured using a flame Atomic Absorption Spectrometry (Varian, SpectrAA-400 Plus, Varian Inc., Australia).

Moreover, heavy metals availability was assessed with soil and plants analyses and with the use of the soil – to – plant transfer coefficient index, (TC = C_{plant} / C_{soil}).

The data were analyzed by using Statgraphics plus 8.1. In order to identify significant differences among average values, we employed one-way ANOVA, and performed Duncan's multiple range test at the level of significance of 95% (p < 0.05).

3. RESULTS AND DISCUSSION

3.1. Soil properties

Table 2. Soil properties and heavy metals concentration of contaminated soil

	Contaminated Soil
pH	8.1
CaCO₃	5.5%
Organic Matter (O.M.)	1.5%
Sand	38%
Silt	45%
Clay	17%
Cu	32.5ppm
Cr	180.4ppm

Ni	159.1ppm
Zn	62.3ppm
Pb	9.9ppm

The physicochemical properties and the heavy metals content of the used soil in the experiment, are shown in Table 2.

The soil which used was loam (L) (silt 45%, clay 17% and sand 38%) with an alkaline pH (8.1), total CaCO₃ equivalent of 5.5% and low organic matter content of 1.5%. The heavy metals content of the used soil were Pb=9.9 mg kg⁻¹, Zn = 62.3 mg kg⁻¹, Cu = 32.5mg kg⁻¹, Ni = 159.1mg kg⁻¹ and Cr = 180.4mg kg⁻¹, Cd not detected.

3.2. Pseudo-total content of heavy metals in soil samples

Table 3. Total heavy metals concentration of collected soil samples (mg Kg⁻¹)

Treatment	Cu	Zn	Pb	Ni	Cr	Cd
Concentration of heavy metals in soil (mg / kg of soil)						
CS.M1.TD	22.40^a	59.90 ^a	7.00 ^{ab}	171.00 ^{bc}	205.1 ^e	ND*
CS.M2.TD	23.25 ^{ab}	62.91 ^{bc}	7.15 ^b	165.50^a	182.25 ^c	ND*
CS.M3.TD	25.36 ^d	62.30 ^{bc}	6.74^a	176.12 ^d	171.16 ^b	ND*
CS.M4.TD	23.40 ^{ab}	59.64^a	6.82 ^{ab}	173.83 ^{cd}	169.62 ^b	ND*
CS.M5.TD	23.90 ^{bc}	60.96 ^{ab}	7.00 ^{ab}	169.00 ^{ab}	170.76 ^b	ND*
CS.M6.TD	24.74 ^{cd}	62.95 ^{bc}	7.64 ^c	168.68 ^{ab}	159.07^a	ND*
CS.TD	24.25^{bc}	63.75^c	11.8^d	195.46^e	189.45^d	ND*

* ND: Not Detected

* Different letters at each column denote statistically significant different means (F-test, P < 0.05); data which presented are mean values.

According the Table 3, the mixture of manure and attapulgit in the soil at three different levels has different effect on the reduction of heavy metals in the soil. In the case of Copper (Cu) the highest reduction came from the mixture 25% manure and 75% attapulgit at the 3% level. The mixture 50% manure and 50% attapulgit at the 3% level has the most positive effect in the Nickel (Ni) reduction and in the case of Lead (Pb) the highest reduction came from the mixture 75% manure and 25% attapulgit at the 3% level, The 4% level has positive effect in the reduction of Zinc (Zn) and of Chromium (Cr). The highest reduction in Zinc and in Chromium came from the mixture 25% manure and 75% attapulgit and from the mixture 75% manure and 25% attapulgit, respectively.

Also, Lead was the heavy metal that had the greatest reduction in soil from the use of the different soil amendments (average 38.8%).

3.3. Total content of heavy metals in *Triticum durum* plants

Table 4. Total heavy metals concentration of collected plants samples (mg Kg^{-1})

Treatment	Cu	Zn	Pb	Ni	Cr	Cd
	Concentration of heavy metals in <i>Triticum durum</i> plants (mg / kg dry weight of plant)					
CS.M1.TD	7.83 ^b	18.32^a	0.19723 ^f	1.597 ^d	2.54 ^e	ND*
CS.M2.TD	10.40 ⁱ	23.41 ^d	0.20785 ⁱ	1.740 ⁱ	2.38 ^c	ND*
CS.M3.TD	7.40^a	24.89 ⁱ	0.19646 ^c	1.614 ^f	2.12^a	ND*
CS.M4.TD	8.88 ^d	24.25 ^e	0.19493^a	1.580 ^b	2.60 ^f	ND*
CS.M5.TD	8.18 ^c	24.42 ^f	0.19685 ^e	1.595 ^c	2.45 ^d	ND*
CS.M6.TD	9.25 ^e	22.51 ^c	0.19655 ^d	1.560^a	2.28 ^b	ND*
CS.TD	9.38^f	20.22^b	0.19645^b	1.607^e	2.68ⁱ	ND*

* ND: Not Detected

* Different letters at each column denote statistically significant different means (F-test, $P < 0.05$); data which presented are mean values.

The addition of a soil amendment mixture of manure and attapulgit reduced the concentration of heavy metals in *Triticum durum* plants. The comparison between the treatment CS.TD (contaminated soil plus *Triticum durum* plant without soil amendment) and the treatments with the soil amendment addition, showed that the Copper and Chromium reduction was higher in the mixture 75% manure and 25% attapulgit at the 3% level, the Zinc reduction was higher in the mixture 25% manure and 75% attapulgit at the 3% level, the Lead and the Nickel reduction was higher in 25% manure and 75% attapulgit and in 75% manure and 25% attapulgit at the 4% level, respectively.

3.4. The transfer coefficient index, ($TC = C_{\text{plant}} / C_{\text{soil}}$)

Table 5. The transfer coefficient index, ($TC = C_{\text{plant}} / C_{\text{soil}}$)

Treatment	Cu	Zn	Pb	Ni	Cr	Cd
	The transfer coefficient index, ($TC = C_{\text{plant}} / C_{\text{soil}}$)					
CS.M1.TD	0.350	0.306	0.02820	0.00930	0.01238	ND*
CS.M2.TD	0.447	0.372	0.02905	0.01050	0.01310	ND*
CS.M3.TD	0.304	0.400	0.02915	0.00916	0.01239	ND*
CS.M4.TD	0.379	0.407	0.02860	0.00909	0.01530	ND*
CS.M5.TD	0.342	0.401	0.02810	0.00940	0.01435	ND*
CS.M6.TD	0.374	0.358	0.02570	0.00925	0.01433	ND*
CS.TD	0.387	0.317	0.01660	0.00820	0.01410	ND*

* ND: Not Detected

In the case of Copper (Cu) the Soil – to – Plant Transfer Coefficient was lower in the mixture 75% manure and 25% attapulgite at the 3% level. The mixture 25% manure and 75% attapulgite at the 3% level gave better results in the Zinc (Zn) Soil – to – Plant Transfer Coefficient. The results of the TC index in Lead (Pb), Nickel (Ni) and in Chromium (Cr) were lower in the mixture 75% manure and 25% attapulgite at the 4% level, in the mixture 25% manure and 75% attapulgite at the 4% level and in the mixture 25% manure and 75% attapulgite at the 3% level, respectively.

4. CONCLUSION

The experimental results indicated that the mixture soil amendment manure – attapulgite could be successfully used for the adsorption of Cu, Zn, Pb, Ni and Cr cations from contaminated soils.

Our studies showed that the mixture of manure and attapulgite in the soil at three different levels has different effect on the reduction of heavy metals in the soil and plants of *Triticum durum*. In soil the highest reduction was observed in Lead using the mixture 25% manure and 75% attapulgite at level 4% (average 38.8%).

It can be said that the mixture manure – attapulgite is a promising material that can be used successfully for the remediation of toxic heavy metals. Of course, it needs to be done further experiment of the specific soil improvements.

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