

## **ASSESSMENT AND MANAGEMENT OF HEAVY METAL CONTAMINATION OF AGRICULTURAL SOILS IN LARISSA, GREECE, BY USING ENVIRONMENTALLY FRIENDLY MATERIALS**

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### **Abstract**

*The contamination of agricultural soils by heavy metals has aroused considerable apprehension worldwide due to their toxicity and persistence. In this study, the contamination with cadmium (Cd), lead (Pb), nickel (Ni), copper (Cu), chromium (Cr) and Zinc (Zn) in agricultural soils from two regions of Larissa (first region: agricultural soils with application of sewage sludge, second region: agricultural soils near large motorways) was assessed by collecting soil samples as well as by using appropriate contamination indices. The soil sample with the highest metal contamination, was used in pot experiment. The purpose of the experiment was to evaluate the effectiveness of treatment with a mixture of 50% manure and 50% attapulgite at three different levels (0%, 3% and 4% mix of manure - attapulgite / Kg soil) to reduce the availability of the pollutants to Quinoa (*Chenopodium*) plants. The agricultural soil samples were analyzed for their physicochemical properties and for "pseudo-total" heavy metals content after their extraction with boiling Aqua Regia and by using the atomic absorption spectrophotometer. The level of soil pollution was assessed by using Contamination Factor (CF) and Pollution Load Index (PLI). According to the PLI results, the agricultural soils both of two study regions of Larisa, was strongly polluted. Particularly, the CF results revealed that the first study region was very high contaminated with Cr and the second study region was significant and very high contaminated with Ni and Cr, respectively. The results of the pot experiment indicated that, the addition of mixture of manure and attapulgite reduces the uptake of metal pollutants by plants, confirming the possibility of using this mixture in amendment treatments of metal-contaminated soils.*

**Keywords:** heavy metals, agricultural soil, pollution, contamination indices, quinoa, attapulgite

### **1. INTRODUCTION**

Soils contaminated with heavy metals (HMs) have become one of major environmental problems around the world (Islam *et al.*, 2016), as soil constitutes a crucial component of rural and urban environments and can be considered as a very important "ecological crossroad" in the landscape (Zhongmin *et al.*, 2018). The contamination may occur mainly arise as a consequence of a range of anthropogenic activities, such as the industrial expansion, road traffic and agricultural practices: application of chemical fertilizers, pesticides and sewage sludge (Liu *et al.*, 2018). Agricultural practices may accumulate high levels of potentially heavy metals in soils, creating a problem of safe rational utilization of agricultural soil. As a result, excessive accumulation of HMs in agricultural soils may not only result in soil contamination, but also affect food quality and safety (Bi *et al.*, 2018; Huang *et al.*, 2018).

The most common heavy metals found in soils sites are cadmium (Cd), lead (Pb), nickel (Ni), copper (Cu), chromium (Cr) and Zinc (Zn) (Argiri & Tsadilas, 2015; Argiri *et al.*, 2021). These heavy metals are absorbed through the root systems and induce deleterious effects in most of the plants. Although some trace elements are essential in plant nutrition, plants growing in contaminated soils increased concentration of heavy metals, enough to cause clinical problems both to animals and human beings consuming these metal-rich plants as there is no good mechanism for their elimination from the human body. Most metals may persist in soils for a long time after their introduction because they not undergo microbial or chemical degradation (Huang *et al.*, 2018; Briffa *et al.*, 2020). To sustain the

agricultural environment, it is necessary to alleviate the toxicity of heavy metals from the environment.

In Greece, there are a few known contaminated areas, mainly located around former mining explorations (Kirki, Pb/Zn mines, north Greece; Lavrio, Pb/Zn mines, south of Athens; Drama, Mn mines, north Greece), and in industrial areas of main cities (Thriasio plain in Athens; Sindos in Thessaloniki) (Antoniadis *et al.*, 2019). However, there are some areas which are suspected contaminated but have not been adequately investigated. One such area is the rural area of Larisa (Skordas *et al.*, 2010; Argiri & Tsadilas, 2015). The area has the unique features of being (a) used continuously for centuries for food crop production, and (b) there is in the vicinity of various activities that would result in HMs enrichment. Anthropogenic activities potentially affecting the area concerning HMs contamination are primarily (a) the intensive cultivation of agricultural land, along with the irrational use of fertilizers or the application of sewage sludge and (b) the passage of large motorways along cultivated soils.

Considering that soils are not a renewable resource and that heavy metals do not biodegrade but accumulate in soils, it is necessary to monitor soil metal concentrations to prevent pollution situations and to propose remediation actions if necessary.

Various technologies were evolved to clean up heavy metals from soil but, in the recent years scientists have begun to study more cost-effective and environmentally friendly technologies, including the use of organic and inorganic soil improvements such as manure and attapulgite, respectively (Uddin, 2017; Provolo *et al.*, 2018). Attapulgite is an aluminosilicate mineral, which was found in abundance in the Greek subsoil (Zotiadis *et al.*, 2012). The use of attapulgite and manure as soil improvements, is a promising strategy for soil remediation through the change in mobility and bioavailability of heavy metals (Falayi & Ntuli, 2015; Provolo *et al.*, 2018). However, their beneficial effects as soil improvements have not been studied extensively (Zotiadis *et al.*, 2012). Moreover, open to research remains the quest for the most effective mixing proportions of the two materials, as an attempt to increase the stabilization of heavy metals in the soil and to create the necessary conditions for proper development of plants.

Also, it is important to study crops that have the ability to survive under the problem soils, such as quinoa (*Chenopodium quinoa* Willd.) (Hinojosa *et al.*, 2018). Due to its high nutritional profile and wide range of adaptability under stress conditions it could be best option for food security (Rizvi *et al.*, 2018). Quinoa can tolerate combination of abiotic stresses like high temperature, drought, salinity and frost. However, studies of other important factors of stress such as tolerance to heavy metals are very limited (Hasseb *et al.*, 2018).

Thus, the objectives of this study was: (1) to determine the total concentration of Cd, Cr, Ni, Zn, Pb, Cu, in soils around the Larisa area, (2) to determine the capacity of mixture of manure and attapulgite that effectively can limit the heavy metals concentration in the soil and (3) to study the possibility of safe cultivation of quinoa plants in contaminated soils using modified soil improvement.

## **2. MATERIALS AND METHODS**

### *2.1. Study Area*

Larisa is the studied area, and specifically two regions of Larissa with agricultural soils which are used continuously for centuries for food crop production. First region is located approximately 20 km (Rodia - Deleria villages) from Larisa city, Greece. In this rural area, many farmers apply sewage sludge to fertilize their crops.

Second region is an area near the city, where exists the national highway which connects Larisa to Athens. The most selected soils were cultivated fields at the immediate vicinity of the national highway. Also, in the second study region, there is a factory which produces aluminum/metal products.

The reasons that we selected these regions were a) the normal highly intensive agricultural activities

carried out which in addition, are include apply sewage sludge and b) the vicinity to the above mentioned suspected polluting sources.

Finally, the area of Larisa has a typical Mediterranean climate with wet and cold winters and dry and hot summers.

## 2.2. Soil sampling

From the two study areas of Larisa 25 composite soil samples (12 from the first and 13 from the second region), were collected. Specifically, three soil subsamples were obtained from the perimeter of a circle of 40-to-50-cm radius from random positions in each study area. The three subsamples were merged into one composite sample and thoroughly homogenized. These 25 composite soil samples were obtained from a depth of 0–5 cm from the soil surface, using a steel sampler. With a Hand GPS the coordinates (latitude, longitude) were taken for every soil sample. Then, using the ArcGIS program, digital maps were made showing the concentrations of heavy metals.



**Fig. 1.** Digital map of the Chromium (Cr) concentrations in the studied areas (a) first area, (b) second area



**Fig. 2.** Digital map of the Copper (Cu) concentrations in the studied areas (a) first area, (b) second area



**Fig. 3.** Digital map of the Nickel (Ni) concentrations in the studied areas (a) first area, (b) second area



**Fig. 4.** Digital map of the Lead (Pb) concentrations in the studied areas (a) first area, (b) second area



**Fig. 5.** Digital map of the Zinc (Zn) concentrations in the studied areas (a) first area, (b) second area

### 2.3. Methods

The collected soil samples were air-dried at room temperature, disaggregated in a ceramic pestle and mortar, and sieved through a 2 mm sieve to remove stones and pebbles. Each soil sample received a unique code. The <2 mm fraction of the soil was used for all soil analyses.

The below physicochemical properties were analyzed: pH (1:2.5 H<sub>2</sub>O), CaCO<sub>3</sub> (Bernard densitometer), electrical conductivity (1:1 H<sub>2</sub>O), particle size distribution (Bouyoucos hydrometer), and organic matter (Walkley – Black wet oxidation). Also, the samples were analyzed for their “pseudo-total” heavy metals content (Cr, Cu, Cd, Zn, Pb, Ni) by *aqua regia* (digestion at 140 °C for 5 hours with 3:1 concentrated HCl: HNO<sub>3</sub>) (ISO/DIS 11466, 1994). The concentrations of total metals in the supernatant liquid were measured with a flame Atomic Absorption Spectrometry (Varian, SpectrAA-400 Plus, Varian Inc., Australia). All soil samples were treated in duplicate. In all cases, standards (stock standard solution of 1000 mg/l concentration) and blank were treated in the same way as the real samples to minimize matrix interferences during analysis.

The level of soil pollution was assessed by using suitable indices such as the Contamination factor (CF) and the pollution load index (PLI). Additionally, according to the obtained results of the *aqua regia* extraction, the soil sample with the highest heavy metal concentration was used to conduct a pot experiment in a greenhouse. Specifically for the experiment, a quantity of ca. 50kg soil was be collected from a depth of 0 – 30 cm from field which exhibited the highest metal concentration (CS). The soil type waw be air dried, sieved with a stainless steel sieve (15 mm hole size) and used to fill the pots (4 kg soil per pot). Treatments were included a mixture of manure and attapulгите (50% manure and 50% attapulгите) applied in the soil at three different levels (0%, 3% and 4% mixture of manure - attapulгите / Kg soil) and quinoa crop. In each pot 20 quinoa seeds was be sown to a depth of 2,5 cm. The treatments, which are presented in the Table 1, were repeated four times and the pots were arranged in a randomized design in the greenhouse. The plants were grown for 120 days, after germination. During the experiment weeds, pests and / or diseases were controlled appropriately, and 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 80 ° C, weighted and ground to <2 mm. Total concentration of Cd, Pb, Ni, Cu, Cr and Zn in the plants were assessed using the dry ash method (Jones and Case (1990)). The “pseudo” total concentration of metals in the soil, after plant cultivation and the incorporation of soil improvements was determined following the same methodology as above.

**Table 1.** Treatments of the pot experiment

Code	Treatment
CS.Q	4 kg soil from the second study area with the highest heavy metals concentration plus Quinoa
CS.M1.Q	4 kg soil from second study area with the highest heavy metals concentration plus mixture of 50% manure – 50% attapulgit (3% mixture / kg soil) plus Quinoa
CS.M2.Q	4 kg soil from second study area with the highest heavy metals concentration plus mixture of 50% manure – 50% attapulgit (4% mixture / kg soil) plus Quinoa

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<sub>plant</sub> / C<sub>soil</sub>).

After laboratory analyses, the raw data was be processed and statistically evaluated. The results 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

Data on physicochemical properties and pseudo-total elemental concentrations in soil samples from the two studied areas, are presented in Tables 2, 3, 4 and 5.

**Table 2.** Physicochemical properties of collected soil samples in first study area of Larisa

Code of soil sample	pH	Electrical conductivity (µS/cm)	CaCO <sub>3</sub> (%)	Organic matter (%)	Sand (%)	Clay (%)	Silt (%)
1	7.0	170	1.5	1.4	29	23	48
2	6.5	86	1	1.2	28	25	47
3	7.1	142	1	1.4	26	27	47
4	7.4	192	1	2.7	32	21	47
5	7.4	331	1.5	3.0	30	19	51
6	7.3	115	1.5	1.3	38	17	45
7	7.4	163	1.5	1.9	34	25	41
8	6.7	90	1	0.9	34	25	11
9	6.8	128	1.5	1.1	44	19	37
10	7.0	146	1	1.5	32	27	41
11	7.2	135	1.5	1.8	33	21	46
12	6.5	140	1.5	1.9	30	25	45
<b>Range</b>	<b>6.5 – 7.4</b>	<b>86 - 331</b>	<b>1 – 1.5</b>	<b>0.9 - 3</b>	<b>26 - 44</b>	<b>17 - 27</b>	<b>11 - 51</b>
<b>Mean</b>	<b>7</b>	<b>153.2</b>	<b>1.3</b>	<b>1.7</b>	<b>32,5</b>	<b>22,8</b>	<b>42,2</b>
<b>SD</b>	<b>0.3</b>	<b>63.8</b>	<b>0.3</b>	<b>0.6</b>	<b>4,8</b>	<b>3,4</b>	<b>10,5</b>

According to Table 2, pH ranges between 6.5 - 7.4 (average 7), electrical conductivity (EC) between 86 - 331  $\mu\text{S}/\text{cm}$  (average 153.2),  $\text{CaCO}_3$  between 1 - 1.5% (average 1.3), organic matter between 0.9 - 3% (average 1.7), sand between 26 - 44% (average 32.5), clay between 17 - 27% (average 22.8) and silt between 11 - 51 (average 42.2).

**Table 3.** Physicochemical properties of collected soil samples in second study area of Larisa

Code of soil sample	pH	Electrical conductivity ( $\mu\text{S}/\text{cm}$ )	$\text{CaCO}_3$ (%)	Organic matter (%)	Sand (%)	Clay (%)	Silt (%)
13	8.1	648	5.5	1.5	38	17	45
14	7.3	531	1	1.5	18	47	35
15	8.3	662	1	1.4	17	53	30
16	8.1	424	4.5	1.3	23	45	32
17	7.1	432	1	2.6	21	51	28
18	7.9	535	1.5	2.1	19	43	38
19	7.7	277	1.5	2.1	59	29	12
20	7.8	434	1.5	1.5	37	39	24
21	7.7	456	1	1.6	24	43	33
22	7.8	427	1.5	2.1	20	52	28
23	7.9	508	4.5	1.5	20	43	37
24	8.1	524	1.5	1.2	19	45	36
25	7.7	492	1.5	1.4	25	42	33
<b>Range</b>	<b>7.1 - 8.3</b>	<b>277 - 662</b>	<b>1 - 5.5</b>	<b>1.2 - 2.6</b>	<b>17 - 37</b>	<b>17 - 53</b>	<b>12 - 45</b>
<b>Mean</b>	<b>7.8</b>	<b>488.5</b>	<b>2.1</b>	<b>1.7</b>	<b>26.2</b>	<b>42.2</b>	<b>31.6</b>
<b>SD</b>	<b>0.3</b>	<b>100.4</b>	<b>1.6</b>	<b>0.4</b>	<b>11.9</b>	<b>9.8</b>	<b>7.9</b>

According to Table 3, pH ranges between 7.1 - 8.3 \*average 7.8), EC between 277 - 662  $\mu\text{S}/\text{cm}$  (average 488.5),  $\text{CaCO}_3$  between 1 - 5.5% (average 2.1), organic matter between 1.2 - 2.6% (average 1.7), sand between 17 - 37% (average 26.2), clay between 17 - 53% (average 42.2) and silt 12 - 45% (average 31.6).

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

We measured 6 HMs in order to identify the level of contamination of the two study regions of Larissa.

According to Table 4, Cd was not detected in agricultural soils of first study area, in Larisa. Total Cr concentration ranged between 9.6 - 15.3 ppm, total Cu between 14.1 - 32.1 ppm, total Ni between 8.3 - 15.3 ppm, total Pd between 5.7 - 11.1 ppm and total Zn between 25.2 - 65.1 ppm. According to Council of the European Communities (1986), the soil of the first study area was contaminated with Cr.

**Table 4.** Heavy metals concentration of collected soil samples in first study area of Larisa

Code of soil sample	Pseudo-total concentrations of heavy metals ( $\text{mg kg}^{-1}$ )					
	Cd	Cr	Cu	Ni	Pb	Zn
1	ND*	103.1	14.7	13.8	6.7	43.2
2	ND*	89.4	13.8	13.4	7.6	41
3	ND*	108.0	14.5	15.3	10.7	49.3
4	ND*	99.0	17.9	14.7	9.1	50.5
5	ND*	100.3	32.1	14.4	11.1	65.1

6	ND*	100.4	26.5	9.6	7.1	44.7
7	ND*	110.4	23.3	12	8.6	48.6
8	ND*	93.6	14.1	8.3	5.7	25.2
9	ND*	110.5	21.4	10.1	8.4	49.6
10	ND*	105.0	19	12.5	7.2	40
11	ND*	80.4	20.2	12.7	8	41
12	ND*	130.0	24	13.2	8.9	43.1
<b>Range</b>	-	<b>80.4 – 130.0</b>	<b>14.1 – 32.1</b>	<b>8.3 – 15.3</b>	<b>5.7 – 11.1</b>	<b>25.2 – 65.1</b>
<b>Mean</b>	-	<b>102.5</b>	<b>20.1</b>	<b>12.5</b>	<b>8.3</b>	<b>45.1</b>
<b>SD</b>		<b>12.4</b>	<b>5.7</b>	<b>2.2</b>	<b>1.6</b>	<b>9.2</b>
<b>EU</b>	<b>1– 3</b>	-	<b>50 - 140</b>	<b>30 - 75</b>	<b>40 - 300</b>	<b>150 - 300</b>

\*ND: Not Detected; EU=Limits according to the European Union Directive (CEC, 1986).

Also, according to Table 5, Cd was not detected in agricultural soils of second study area, in Larisa. Total Cr concentration ranged between 65.5 - 180.4 ppm, total Cu between 16.5 - 34.3 ppm, total Ni between 133.2 - 172.8 ppm, total Pd between 6.8 - 11.9 ppm and total Zn between 31.7 - 70.6 ppm. Two HMs of these, were elevated beyond the European Union Directive limits: average value (mg kg<sup>-1</sup>) for Cr was 126.1 vs. 0 of EU Directive limit, and Ni was 156.6 vs. 75. This indicates strong enrichment of soils with Cr and Ni.

**Table 5.** Heavy metals concentration of collected soil samples in second study area of Larisa

Code of soil sample	Pseudo-total concentrations of heavy metals (mg kg <sup>-1</sup> )					
	Cd	Cr	Cu	Ni	Pb	Zn
13	ND*	180.4	32.5	159.1	9,9	62,3
14	ND*	130.2	32.8	159.7	11.2	70.6
15	ND*	141.5	34.3	172.8	11.6	66.9
16	ND*	171.3	31.9	159.8	10.4	60
17	ND*	126.1	31.4	159.9	11.9	66.8
18	ND*	107.8	31.9	159.2	11.4	62.8
19	ND*	65.5	16.5	133.2	6.8	31.7
20	ND*	83.6	26.8	151.1	11.4	52.1
21	ND*	111	28.2	150	10.5	61.2
22	ND*	125	29.2	156	9.6	59.8
23	ND*	132	30.4	158	11.3	60
24	ND*	145	32	157	11.2	60
25	ND*	120	33.2	160	9.8	65.3
<b>Range</b>	-	<b>65.5 – 180.4</b>	<b>16.5 – 34.3</b>	<b>133.2 – 172.8</b>	<b>6.8 – 11.9</b>	<b>31.7 – 70.6</b>
<b>Mean</b>	-	<b>126.1</b>	<b>30.1</b>	<b>156.6</b>	<b>10.5</b>	<b>60</b>
<b>SD</b>	-	<b>31.3</b>	<b>4.6</b>	<b>8.9</b>	<b>1.4</b>	<b>9.6</b>
<b>EU</b>	<b>1– 3</b>	-	<b>50 - 140</b>	<b>30 - 75</b>	<b>40 - 300</b>	<b>150 - 300</b>

\*ND: Not Detected; EU=Limits according to the European Union Directive (CEC, 1986).

The above findings were also confirmed by Contamination factor (CF) and pollution load index (PLI).

Contamination factor (CF) is the ratio obtained by dividing the concentration of metals in soil by their background values:  $CF = CS / C_{RefS}$  (Antoniadis et al., 2017), where CS is total element concentrations in soil and  $C_{RefS}$  is background reference element concentration in uncontaminated soils, as defined by Kabata-Pendias (2011, p. 41). The contamination level may be classified as follows: low degree ( $CF < 1$ ), moderate degree ( $1 \leq CF < 3$ ), significant degree ( $3 \leq CF < 6$ ) and very high degree ( $CF \geq 6$ ) (Antoniadis *et al.*, 2017).

The pollution load index (PLI) allows the levels of soil contamination to be compared between different locations. PLI is the coefficient of concentration of each metal ion in relation to the reference value of the metal in uncontaminated soil. PLI is applied by:  $PLI = (cf_1 \times cf_2 \times cf_3 \times \dots \times cf_n)^{(1/n)}$  where n, the number of studied metals. If  $PLI < 1$  the soil is unpolluted, if  $1 < PLI < 2$  the soil is moderately polluted. if  $2 < PLI < 10$  the soil is strongly polluted, if  $PLI > 10$  the soil is extremely polluted (Moataz Khalifa & Gad, 2018).

The results of the contamination factor and pollution load index, measurement appear in Table 6 and Table 7, respectively.

**Table 6.** Heavy metals contamination factor (CF) of the studied regions.

<b>Study area</b>	<b>Cr</b>	<b>Cu</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>
First	6.03	0.52	0.43	0.31	0.64
Second	7.42	0.60	5.22	0.26	0.40

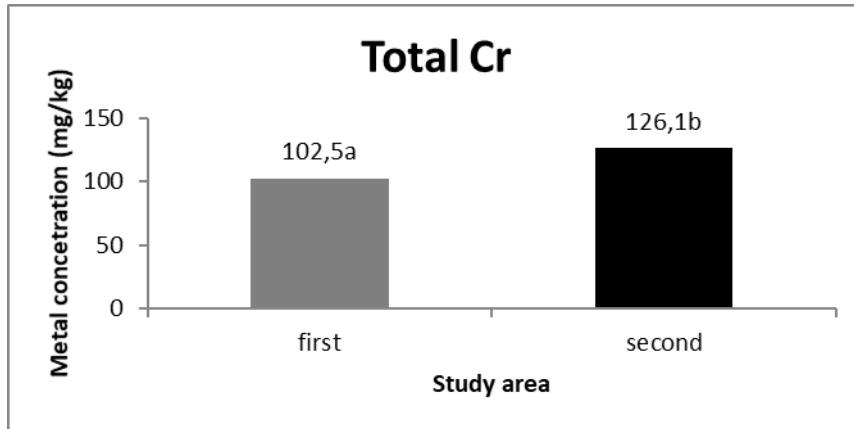
**Table 7.** Pollution Load Index of HMs in studied regions.

<b>Study area</b>	<b>PLI</b>
First	2,59
Second	7,77

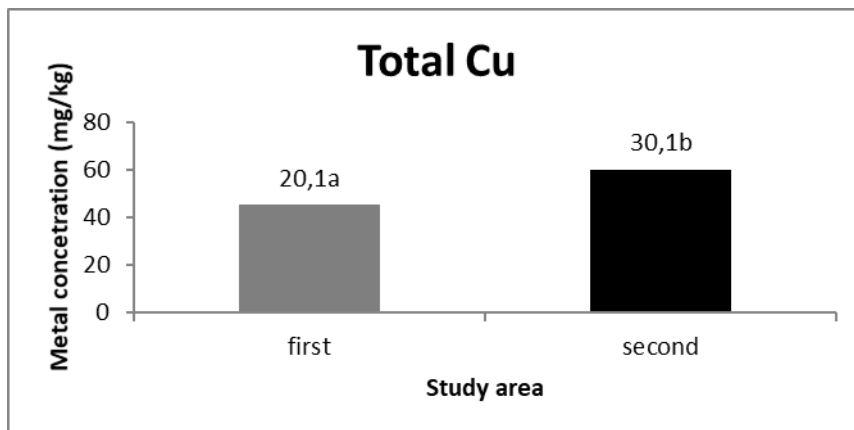
As per contamination factor (Table 6), the first study region, has low contamination due to Cu, Ni, Pb and Zn, but very high contamination due to Cr. The second study region has low contamination due to Cu, Pb and Zn, but significant and very high contamination due to Ni and Cr, respectively.

According to the PLI results (Table 7), the agricultural soils both of two study regions of Larisa, was strongly polluted.

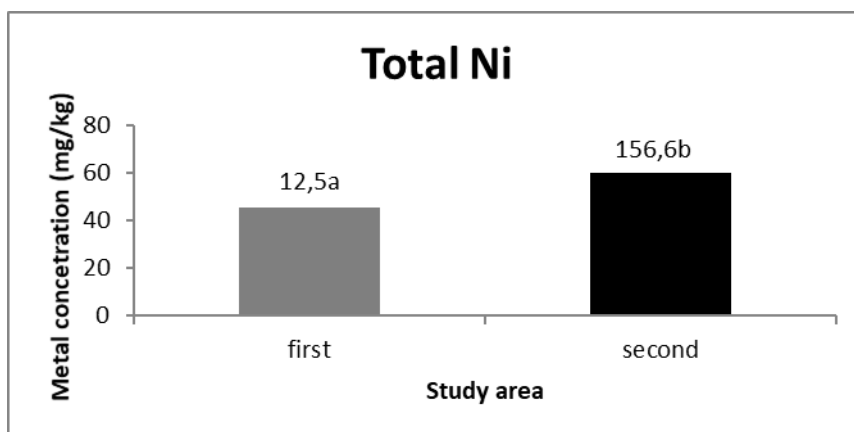
The following graphs (Figure 1 -5) show the comparison of the soil contamination level of the two study areas, for each heavy metal, separately.



**Fig. 6.** Average Total Cr concentration (mg/kg) in two studied areas.



**Fig. 7.** Average Total Cu concentration (mg/kg) in two studied areas.



**Fig. 8.** Average Total Ni concentration (mg/kg) in two studied areas.

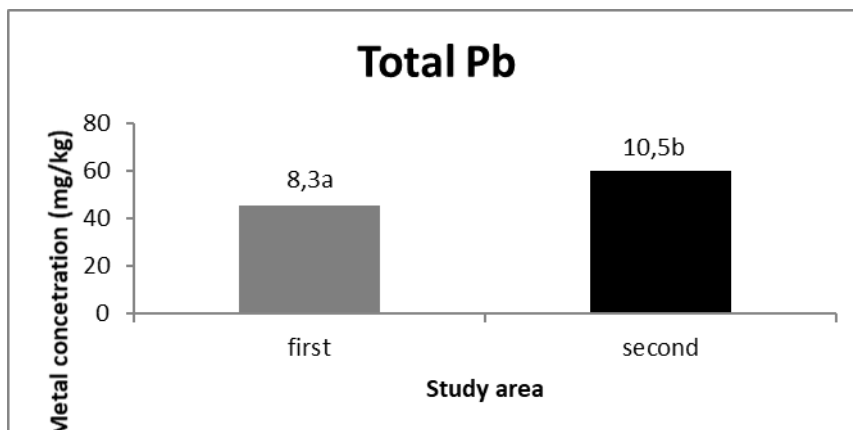


Fig. 9. Average Total Pb concentration (mg/kg) in two studied areas.

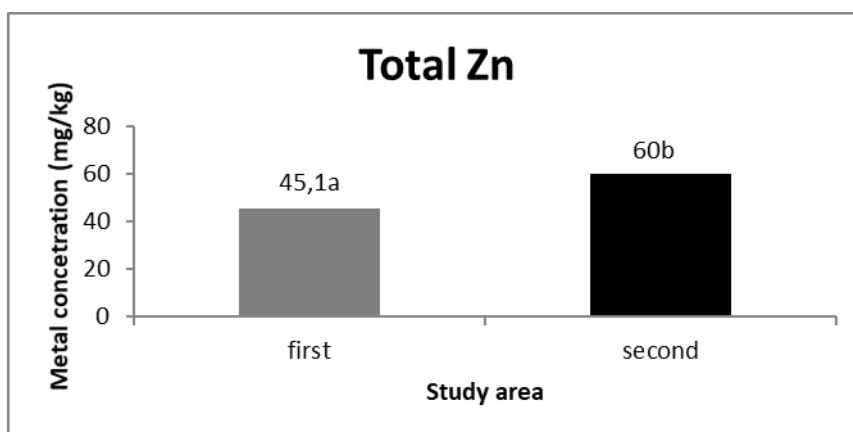


Fig. 10. Average Total Zn concentration (mg/kg) in two studied areas.

According to Figure 6 to 10, between the two studied areas (first and second) there is a statistically significant difference in total chromium, copper, nickel, lead, and zinc concentration (Significant at the level of  $p < 0.05$ ). The *aqua regia* extracted concentrations of studied HMs are higher in the agricultural soil of the second study area, which is located near a national highway and a metal products factory.

### 3.3. Total content of heavy metals in soil samples

**Table 8.** Concentration of heavy metals in soil (mg / kg).

Treatment	Concentration of heavy metals in soil (mg / kg)				
	Cr	Cu	Ni	Pb	Zn
CS.Q	233.5c*	24.35c	184c	10.5c	59.9c
CS.M1.Q	230.3b	23.65a	181.5a	10.4a	59.2a
CS.M2.Q	220.35a	23.70b	183b	10.43b	59.63b

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

According to Table 8, between the treatments in every concentration of the studied heavy metals in the soil there was a statistically significant difference. The use of a mixture of 50% manure - 50% attapulgite at 3% level had better results in the reduction of Copper, Nickel, Lead and Zinc. On the other hand, the reduction of Chromium was higher in the treatment in which used the soil amendment 50% manure - 50% attapulgite at 4% level.

### 3.4. Total content of heavy metals in quinoa plants

**Table 9.** Concentration of heavy metals in quinoa plants (mg / kg dry weight of plant).

Treatment	Concentration of heavy metals in quinoa plants (mg / kg dry weight of plant)				
	Cr	Cu	Ni	Pb	Zn
CS.Q	14.5c*	25.3c	19.8f	1.8e	120.2f
CS.M1.Q	8.4b	8.6a	6.8b	0.8b	47a
CS.M2.Q	5.4a	13.1b	5.6a	0.7a	59.6b

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

According to Table 9, the concentration of the studied heavy metals in quinoa plants was statistically significant different between the three treatments.

Particularly, the reduction of the concentration of Cr (average concentration 5.4 versus 8.4 mg / Kg DW), Ni (5.6 vs. 6.8 mg / Kg DW) and Pb (0.7 vs. 0.8 mg / Kg DW) was higher in comparison to the application of the mixture at 4% / Kg of soil. On the contrary, the reduction of the concentration of the Cu (8.6 vs. 13.1 mg/Kg DW) and of Zn (47 vs. 59.6 mg/Kg DW) was higher in the mixture at 3% / Kg of soil.

## 4. CONCLUSION

Soil plays an important role in the biosphere. Heavy metals when they are in high concentration in soils can adversely affect the food chain and the human health.

In this thesis two areas in the region of Larissa have been studied. From the studied heavy metals the only one that not have been detected in the soil samples in both areas was Cadmium (Cd).

In the second studied area where in near in the national highway which connects Larisa to Athens and also there is a factory which produces aluminum/metal products the concentrations of Chromium and Nickel are under the limits that the European Union Directive (CEC, 1986) sets. Furthermore, Chromium concentration was too high in the soil samples which collected from the first region that is located approximately 20 km (Rodia - Deleria villages) from Larisa city, Greece and in this region many farmers apply sewage sludge to fertilize their crops.

Between the two areas there was statistically significant difference in the total heavy metals content.

The contamination factor (CF) in the first study region has low contamination due to Cu, Ni, Pb and Zn, but very high contamination due to Cr. The second study region has low contamination due to Cu, Pb and Zn, but significant and very high contamination due to Ni and Cr, respectively.

According to the PLI results, the agricultural soils both of two study regions of Larisa, was strongly contaminated.

In the second part of the experiments which was used the most contaminated soil from all the samples which were analyzed for the five heavy metals, the different mixtures of the soil amendment had different affection in the rehabilitation of the contaminated soil.

For all the above, more investigations should be done in regions which there is reason to be believed that there is heavy metals contamination because of the human activities.

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