REMOVAL OF SOME HEAVY METALS FROM THE OLD AND NEWLY RECLAIMED LAND.

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ABSTRACT

The environment is becoming more and more contaminated, and using physicochemical processes to clean it up is quite expensive. Consequently, it is crucial to use plants as a technique to remove contaminants. The present study aims to use some plants as *Helianthus annuusL*, *Phragmites australis and Cyperus* to remove some metals Such as Lead (Pb) and Chromium (Cr) from soil depending on their ability to absorb these heavy metals. This is achieved by cultivating the previous plant types in pots (capacity 2 kg) using three types of soil from three areas: Wadi Al-Shagb and Al- Sebiya belonging to Al-Nasr Mining Company in Aswan Governorate, which are reclaimed lands between the phosphate mines, the third soil is taken from Bahteem Agricultural Research Station in Qalyubia Governorate.

The plants were harvested after three periods.i.e,30,45 and 60 days from cultivation through bout 25 pots form each sample .

The ability of Lead and Chromium absorption by plants were evaluated using AAS (Atomic Absorption Spectroscopy). The results revealed highest amount of Lead was found in *Helianthus annuusL* roots 29.80 (ppm) over 60 days, the lowest amount in *Cyperus* roots 3.56 (ppm) over 45 days, the highest amount of Chromium in *Helianthus annuusL* roots 45.60 (ppm) over 60 days, and the lowest amount in *Helianthus annuusL* roots 0.85 (ppm) over 30 days. The highest amount of Lead in the shoots of *Cyperus* 7.34 (ppm) over 60 days and the lowest amount in the shoots of *Cyperus* reached 2.22 (ppm) over 30 days, the highest amount of Chromium in the shoots of *Cyperus* 20.10 (ppm) over 30 days and the lowest amount in *Helianthus annuusL* shoots 8.03 (ppm) over 30 days, also the percentage removal of the metals of the three soils in the range of 91.39 % − 97.11 % for Lead (Pb) and 89.32 % − 98.00 % for Chromium (Cr). Moreover, this study revealed that (*Helianthus annuusL,* and *Cyperus*) are the highest types of excessive accumulation and removal of Lead and Chromium, and they can be used to remove these elements from the old and newly reclaimed lands.

Keywords: Heavy metal; Removal; Plant; Soil; Lead; Chromium.

INTRODUCTION

One of the main environmental problems that humanity has to deal with is soil pollution. The majority of the hazardous metals released into the environment by human activity come from the soil (Rahman *et al*., 2013). As a result, one of the environmental issues is soil. Heavy metals can come from natural sources, or they can be leached from rocks and soil, application of fertilizers or they can come from anthropogenic sources.

Toxic metals introduced into the environment are primarily absorbed by soils. because of the anthropogenic actions listed above. Regardless of where the metals in the soil came from, extreme concentrations of several metals can cause the soil to become less fertile and produce inferior agricultural products, which poses a serious threat to the health of people, animals and Ecosystems (Blaylock and Huang, 2000; and Luo *et al*., 2005).

Metals such as, Lead and Chromium are particularly important since high quantities of these metals can decrease crop production due to the risk of bio magnifications and bioaccumulation in the food chain. There is also the risk of underground and surface

water contamination (Nowack., *et al*., 2006); and Schmidt, 2003). When particular conditions are fulfilled, some heavy metals can change from one oxidation state to another, becoming less hazardous (Alkorta and Garbisu,. 2001). However, some heavy metals cannot be eliminated physiologically species of plants., development stage, soil type, metals, and environmental factors frequently affect how hazardous metals are absorbed by plants Metal availability to plants is significantly influenced by the level of hazardous metal content in the soil solution (Maimon *et al.,* 2009). It entailed metal removal by plants via uptake and accumulation in biomass (Ghosh and Singh, 2005).

Interestingly, although humans recognised and documented phytoremediation a little over 300 years ago, scientific research and development did not begin until the

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early 1980s (Lasat, 1999). However, the absence of methods to maximize plant uptake of metals has slowed down efforts to turn phytoextraction into a workable commercial technique (Wang *et al.,* 2006).

Traditional methods, including physical, chemical, biological and phytoremediation, can be used to modify contaminated soil unfortunately, current remediation techniques for removing hazardous metals from polluted soils are pricy and inconvenient (Ghosh and Singh, 2005). Recent attempts have concentrated on cleanup techniques that are more affordable, less harmful, and sustainable (Gupta and Sinha, 2007; and Xiaomei *et al.,* 2005). There is a lot of proof linking the contamination of hazardous metals in soil and toxic metals in crops (Syakalima *et al.,* 2001). Using different plants to remove, degradation, containment, or immobilization pollutants from soil and water is a new method called using recently, this approach has drawn a lot of attention as a creative, economical substitute for the more traditional treatment techniques employed at hazardous waste sites (US EPA., 2000). The objective of this study is to see how well *Helianthus annuusL, Phragmites australis,* and Cyperus plants remove Lead (Pb) and Chromium (Cr) from old and newly reclaimed soil. and to assess the efficiency with which these plants remove these metals.

MATERIALS AND METHODS.

Study area:

A pot experiment with 27 treatments (3 plant spices X 3 soil types X 3 harvesting periods) and 25 pots form each type of soil was carried out in experiment green house at tenancy soil in Abu Rawash area, private farm, which is located 8 km north of Giza Governorate in coordinates (″N 30°01′55 -″E 31°04′30). Using pots filled 2 kg capacity from three soil types. The 1st soil sample was taken from wadi al-shaghb (East Nile), while the 2nd sample was taken from Sebaiya (West Nile) both of them affiliated to the Al- Nasr Mining Company in Aswan Governorate. The 3rd soil

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sample was taken from Bahteem Research Station in Qalyubiya Governorate The location of the three studied soil samples are shown in Fig (1).

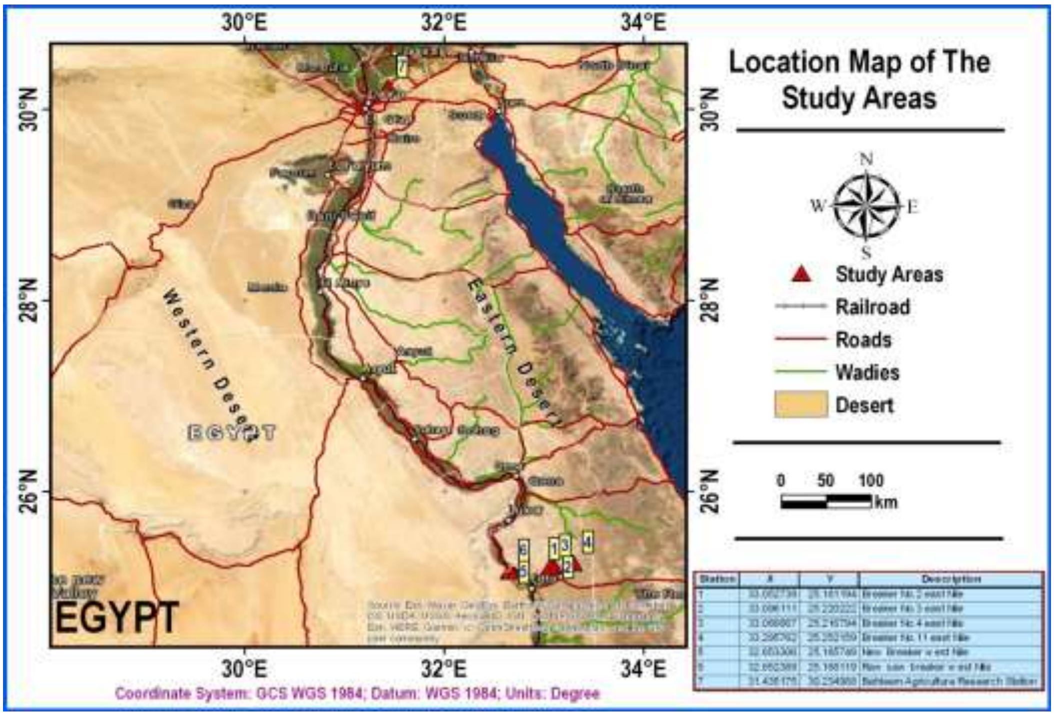

Fig (1): Soil sample location map.

Table (1): Some physicochemical properties of heavy metals of the studied soil before planting.

SOIL LOCATION SOIL PROPERTIES	WADI AL-SHAGHB EAST NILE	SEBAIY AWEST NILE	BAHTEEM
pH	8.05	8.01	7.75
Organic matter (%)	2.13	2.19	3.60
EC(dS/m^{-1})	1.56	1.62	1.69
Moisture (%)	nell	nell	0.02%
Textural class	Sandy loam	Sandy loam	Clay
Pb (ppm).	55	48	104
Cr (ppm).	100	120	85
$CaCO_3$ (%)	11.75	10.91	2.30
P (%)	11.79	10.91	2.30
SO_3(%)	1.99	1.74	1.61

Soil analysis: Determination of heavy metal: weight 1 g of the soil into a 100 ml Teflon beaker with 10 ml of Hydrofluoric Acid (HF), 10ml of Per-chloric acid ($HClO_4$) and 10 ml of concentrated Nitric acid (HNO_3). This mixture was heated at high temperature using a heating mantle (thermostat hotplate, Gallenhamp) until the soil was dried completely. The digested sample was dissolved in 20 ml of 20 % Hydrochloric acid (HCl), filtered into a 50 ml volumetric flask. The filtrate was diluted by ultra - pure water (i.e. water level was made up to the mark), after which the sample was used for the measurement, using AAS spectrometry. The experimental procedures and analytical methods were performed for AAS according to the producer's guide to instrumentation and applications, regarding the guidelines of European Commission (2006), the report of El-Ansary and El-Leboudy, (2015) and Liu *et al*. (2020).

Plant analysis: The plant species were harvested from the three soils after the cultivation period (30,45 and 60) days, the shoot and root samples of the plants studied were rinsed completely with tap water, then distilled water, and dried in an oven at 100 ^{0}C for 30 minutes, then at 60 ^{0}C for 24 hours. The dried plant samples (about 2.0-3.0 g) were ash by heating at 250 ^{0}C for 2 hours and then gradually increasing to 500 ^{0}C. To digest the plant sample, leave it in concentrated Nitric acid (HNO_3) overnight then, heat at 75 ^{0}C, for 1 hour, followed by 100 ^{0}C for 15 min; after cooling, 2 ml of Hydrogen Peroxide (H_2O_2) was added and heated for 15 min. at 100 ^{0}C. The digested plant sample examined using AAS spectrometry methods to identify the elements Cr and Pb (Huang et al., 2004).

Heavy metal concentration measurement by AAS: For metal analysis, three concentrations of a particular metal's standard solution were chosen. Aspirated blank solution was set to zero. For the relationship between absorbance and standard solution concentration, a calibration curve was created. Direct readings from the instruments were acquired for the prepared sample solution. Following formulas were used to calculate:

$$Result = \frac{AAS\ Reading \times Volume.}{Weight.}$$ (Acar, 2022).

Transfer Factor (TF) for plants.

The ratio of a specific metal concentration in a plant component to that in the soil is known as (TF). Therefore, the following connection was used to determine the TF of heavy metals (Satpathy et al., 2014; Payus and Talip, 2014; Proshad *et al.*, 2020).

$$\text{TF (Transfer factor)} = \frac{\text{Concentration of elements in plant}}{\text{Concentration of elements in soil}}$$

The removal effectiveness of each heavy metal was estimated according (Rahman *et al*., 2013). was calculated as follows:

Removal Efficiency (%) $= C_i - C_f / C_i \times 100$

Where C_i is the initial heavy metal concentration (mg/kg) and C_f is the final heavy metal concentration (mg/kg).

RESULTS AND DISCUSSION.

Lead and Chromium concentration in the three studied soil before planting:

Minerals and moist components, which are abundant in a smaller portion of the soil, make up soils. These moist and mineral soil components contain carboxylic and hydroxyl functional groups, which help to create a charge across the soil surface and aid in the retention of metals in the soil. As a result, the metal content rises in a lesser proportion (Mohanty and Mahindrakar, 2011). Based on the results obtained, it was observed that, the order of Lead (Pb) concentration in the three studied soils is Bahteem 104 (ppm) , Wadi Al-shaghb 55 (ppm) and 48 (ppm) of Sebaiya soil .Also the concentration of Chromium (Cr) is as follows 120 (ppm) of Sebaiya soil, Wadi Al-shaghb 100 (ppm) and 85 (ppm) of Bahteem soil for the three soils before planting, as shown in the results shown in Table (2).

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Table (2): The concentration of Lead (Pb) and Chromium (Cr) in the three studied soils before planting.

SOIL LOCATION / CONCENTRATION (PPM)	WADI AL-SHAGHB	SEBAIYA	BAHTEEM
Pb	55	48	104
Cr	100	120	85

In table (2). The value recommended by the Dutch Standard for Chromium is 100 mg kg ,The Chromium content in the soil of Al-Sebaiya was 120 (ppm), which is higher than the permissible limit while the Chromium in the soils of Wadi Al-Shaghb and Bahteem is within permissible limits. The Lead (Pb) concentration differed as it reached 104 (ppm) in Bahteem soil, while the permissible limit for Lead (Pb) according to the Dutch specifications is 85 (ppm). While the value of Lead (Pb) in the soil of Wadi Al-Shaghb was 55 (ppm) and in the soil of Al-Sebaiya was 48 (ppm), and it did not exceed the standard value according to table (3).

Table (3): Maximum allowed levels of heavy metals in plants and soil.

ELEMENTS	* SOIL TARGET VALUES (PPM).	** SOIL INTERVATION VALUES (PPM).	*** PLANTS VALUE PERMITTED (PPM).
Lead	85	530	2
Chromium	100	360	1.3

* Target values are specified to indicate desirable maximum levels of elements in unpolluted soils.
** Intervention when remedial action is necessary; Source: Denneman and Robberse (1990) and Ministry of Housing, Netherland (1994).
*******Source: WHO (1996).

Concentration and Transfer Factor (TF) of Chromium and Lead in soil.

The data obtained from Table (٤) showed that in the soil of Wadi al-Shaghb, the Lead contents were higher in the roots than in the vegetative shoot, while in the Sebaiya soil, no Lead was inferred in the vegetative shoot, while its values were higher in the root, also in Bahteem soil, no Lead was inferred in the shoot.

Vegetative in *Helianthus annuusl* and *Phragmites australis* plants, while it was found in high concentrations in the vegetative and root system of the *Cyperus* plant.

Also, the Chromium contents in the soil of Wadi Al-Shaghb and Sebaiya varied between the roots and the shoots, while in the soil of Bahteem, no evidence that Chromium was found in the shoots in general, except for the *Cyperus* plant, the presence of Chromium in the shoots and roots.

According to Farai *et al.* (2021), if the concentration of Cr in the root is increased, there is an increase in Cr transfer factor. This proves that larger concentrations of Cr are necessary for its efficient translocation from roots to shoots.

The concentration of the metal in the roots may have an impact on the rate of metal translocation to the shoots, Since the plants roots use nutrient intake before other sections, they will acquire more metals than other parts, at least prior to the translocation process.

The capacity of the soil's elements and their solubility in the soil solution determine how well the plant can absorb nutrients. The roots hold the elements after they have moved through the soil. The components enter the cell through the plasma membrane, adhere to the cell wall, and then travel to the components. The canal proteins and/or carrier proteins take up ions (Dökmeci and Adiloğlu. 2020).

The results obtained for the (TF) are shown in Table (4), less than 1.However, it cannot be said that soil is the only source of heavy metals pollution in plants if the (TF) value is more than 1. Heavy metals can enter plants through air deposition or other unidentified causes (Yan et al . 2012). Where the values of the (TF) ranged in the three soils for Lead as follows, it ranged from 0.20 - 0.28 in Wadi al-Shaghb soil, followed by 0.24 - 0.28 in Sebaiya soil, followed by 0.35 - 0.32, while the (TF) for Chromium in the three soils ranged as follows: from 0.31 - 0.63 in the soil of Wadi al-Shaghb, from 0.28 - 0.30 in the soil of Sebaiya, followed by from 0.50 - 0.53, and in order of the (TF) for the plants, *Cyperus* is followed by *Helianthus annuusL* and followed by *Phragmites australis.*

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In relation to this, Zurera *et al.* (1987) noted that, the physical and chemical qualities of soil, plant species, ambient factors, and human activities all influenced the mobility of metals to plants.

These findings are consistent with those of Naggar et al., (2014); and Niţu *et al.*, (2019).

Table (4): Concentration and Transfer Factor (TF) of Chromium (Cr) and Lead (Pb) in the studied plant species in the three soils.

SITE	PERIOD (DAYS)	PLANT ELEMENT	HELIANTHUS ANNUUSL		T.F	PHRAGMITES AUSTRALIS		T.F	CYPERUS		T.F
			shoots	roots		shoots	roots		shoots	roots	
W di Al-Shaghb	٣٠	Cr	7.03	0.85	0.07	n.d	31.24	0.31	20.10	43.81	0.63
		Pb	2.81	n.d	0.05	0.30	4.07	0.07	6.80	8.80	0.28
	٤٥	Cr	n.d	n.d	-	n.d	n.d	-	n.d	n.d	-
		Pb	n.d	8.09	0.14	n.d	0.21	-	6.93	3.56	0.10
	٦٠	Cr	n.d	n.d	-	n.d	n.d	-	n.d	n.d	-
		Pb	n.d	10.11	0.18	n.d	0.29	-	7.21	3.89	0.20
Sebaiya	٣٠	Cr	8.03	12.80	0.17	3.58	n.d	0.02	10.44	24.35	0.28
		Pb	n.d	10.25	0.21	n.d	5.14	0.10	n.d	n.d	-
	45	Cr	12.50	18.80	0.26	4.04	n.d	0.03	12.94	28.55	0.34
		Pb	n.d	11.78	0.24	n.d	6.84	0.14	n.d	n.d	-
	٦٠	Cr	14.87	22.10	0.30	4.36	n.d	0.03	14.75	31.00	0.38
		Pb	n.d	13.87	0.28	n.d	6.99	0.14	n.d	n.d	-
Bahteem	30	Cr	n.d	13.60	0.16	n.d	n.d	-	n.d	n.d	-
		Pb	n.d	4.33	0.04	n.d	9.44	0.09	2.22	21.55	0.22
	45	Cr	n.d	42.80	0.50	n.d	n.d	-	n.d	n.d	-
		Pb	n.d	27.10	0.26	n.d	15.36	0.14	6.80	27.32	0.32
	٦٠	Cr	n.d	45.60	0.53	n.d	n.d	-	n.d	n.d	-
		Pb	n.d	29.80	0.28	n.d	18.30	0.17	7.34	29.66	0.35

n.d : the concentration is less than 50 ppb.

Determination of Chromium (Cr) content.

Highest amount of Chromium 45.60 (ppm) at 60 days in Bahteem soil was found in the roots samples of *Helianthus annuusl* which was almost higher than that of *Cyperus* and more than that of *Phragmites australis* in contrast, the highest amount of Chromium 20.10 (ppm) at 30 days in Wadi al-Shagb soil was found in the shoots samples of *Cyperus* that were higher than that reported in shoots samples *Helianthus annuus* and more than *Phragmites australis* as shown (Table 4).

Chromium was not detected in the different plant parts, which were analyzed at 45, 60 days in Wadi Al Shaghab soil, Also Chromium was not detected in Phragmites australis and Cyperus in Bahtim soil at 30, 45 and 60 days.

The findings of the current study were higher than the study carried out by Liu.,*et al*., (2009)., the Cr concentration in wheat roots (2.55-8.07 mg/kg) was lower than the findings of the current study.

Determination of Lead (Pb) content.

Lead concentration recorded the highest values in Helianthus annuus L root 29.80 (ppm), followed by Cyperus root 29.80 (ppm), followed by Phragmites australis root 18.30 (ppm) in Bahteem soil at 60 days, while Phragmites australis recorded 0.21 (ppm) in Wadi Al-Shaghb soil at 45 days.

No detected of Lead was found in Cyperus in Sebaiya Soil at 30, 45, and 60 days. The accumulation of Lead in the roots and shoots of plants Helianthus annuus L, Phragmites australis and Cyperus in the current study are higher than the result of Lead accumulation in the leaf and root of *B juncea* reported by Choudhury et al.(2016). are 5.6 -5.85 mg/kg dry weight, respectively.

Table (5) shows the removal efficiency of Lead and Chromium in the studied soil. With the passage of time, a significant decrease in the concentration in Lead and Chromium was observed in the three studied soils, as the results showed that the plants used in this study have the ability to remove some heavy elements after different harvesting periods of 30, 45, and 60 days. The percentage of Lead removal from the soil of Wadi Al-Shaghb was 94.72 %, while it reached 91.39% in Al-Sebaiya soil and 97.11% in Bahteem soil, while the removal percentage of Chromium in Wadi Al-Shaghb soil was 98%, 95.28% in Al-Sabaiya soil, and 89.32% in Bahteem soil. In general, with the progression of time, the concentration of both Lead and Chromium in the soil decreased, which indicates an increase in the percentage of removal by plants It is crucial to select plants with the capacity to accumulate and remove Lead and Chromium pollutants from the soil, which is a sound and inexpensive environmental approach.

Table (5): The removal efficiency (R%) of Lead and Chromium in the three soils after harvesting 60 days.

SITE	**LEAD**		**(R%)**	**CHROMIUM**		**(R%)**
	Initial concentration (ppm)	**Final concentration (ppm)**		**Initial concentration (ppm)**	**Final concentration (ppm)**	
Wadi Al-Shaghb	55	2.90	94.72	100	2	98.00
Sebaiya	48	4.13	91.39	120	5.66	95.28
Bahteem	104	*3*	97.11	85	9.07	89.32

CONCLUSION

Heavy metals in soil represent a danger to plants, humans and animals, and it is one of the important environmental issues. In order to minimize the risks involved, of the soil Chromium content, the Lead content in this study was roughly within the permitted limits in soil as indicated by the WHO.

In this study, and through the obtained results, it can be said that the effectiveness of the *Cyperus* plant in removing Lead (Pb) from the soil is the highest, followed by the *Helianthus annuusl* plant, followed by *Phragmites australis* plant, while in removing Chromium (Cr) from the soil, the *Helianthus annuusl* plant was the most effective followed by *Cyperus* plant and then *Phragmites australis* plant.

The values of Lead and Chromium in the plant were higher than allowed Lead (2ppm), Chromium (1.3ppm). Accordingly, it can be concluded that these plants are effective in removing heavy metals and have hyperaccumulation.

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إزالة بعض العناصر الثقيلة (الرصاص والكروميوم) من الأراضي القديمة والمستصلحة حديثا

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المستخلص

أصبحت البيئة أكثر تلوثا، وأصبح أستخدام العمليات الفيزيائية والكيميائية لتنظيفها مكلفا للغاية. وبالتالي من الأهمية استخدام النباتات كتقنية لإزالة الملوثات. تهدف الدراسة الحالية الى إزالة بعض الفلزات مثل الرصاص والكروميوم من الأراضي القديمة والمستصلحة حديثًا وإزالة هذه العناصر باستخدام نباتات (دوار الشمس، السعد، الحجنة) لقدرة هذه النباتات على امتصاص العناصر الثقيلة من التربة ويتحقق ذلك بزراعة الانواع السابقة من النباتات فى اصص (سعة ٢ كجم) باستخدام ثلاثة انواع من التربة المدروسة فى ثلاث مناطق :وادى الشغب والسباعية التابعين لشركة النصر للتعدين بمحافظة اسوان وهم تربة مستصلحة فى نطاق مناجم الفوسفات بينما التربة الثالثة من اراضى محطة بحوث بهتيم الزراعية بمحافظة القليوبية. تم حصاد النباتات على ثلاثة فترات ٣٠، ٤٥ ، ٦٠ يوم من الزراعة بواقع ٢٥ اصيص للنبات الواحد .

تم تقييم قدرة النبات على إزالة الرصاص والكروميوم باستخدام جهاز (التحليل الطيفي للامتصاص الذري AAS). وأظهرت النتائج ان أعلى كمية من الرصاص وجدت فى جذوردوار الشمس ٢٩,٨٠ (جزء فى المليون) على ٦٠ يوم وأقل كمية فى جذور السعد ٣,٥٦ (جزء فى المليون)على ٤٥ يوم ، أعلى كمية من الكروميوم فى جذر دوار الشمس ٤٥,٦٠ (جزء فى المليون) على ٦٠ يوم وأقل كمية فى جذر دوار الشمس ٠,٨٥ (جزء فى المليون على ٣٠ يوم ، أعلى كمية من الرصاص فى المجموع الخضرى فى السعد ٧,٣٤ (جزء فى المليون) على ٦٠ يوم وأقل كمية فى المجموع الخضرى فى السعد ٢,٢٢ (جزء فى المليون) على ٣٠ يوم ، أعلى كمية من الكروميوم فى المجموع الخضرى فى السعد ٢,٢٢ (جزء فى المليون) على ٣٠ يوم وأقل كمية فى المجموع الخضرى فى دوار الشمس ٨,٠٣ (جزء فى المليون على ٣٠ يوم . وبلغت النسبة المئوية لإزالة الفلزات من الترب الثلاثة في حدود ٩١,٣٩٪ – ٩٧,١٪ للرصاص (Pb) و ٨٩,٣٢٪ – ٩٨,٠٠٪ للكروم (Cr).

الكلمات المفتاحية: معادن ثقيلة إزالة; نبات ; تربة ; رصاص; كروميوم .