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Fate of Heavy Metals in Selective Vegetable Plants Irrigated with Primary Treated Sewage Water at Slightly Alkaline Medium

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IT is well known that pH is the controlling factor for solubility of metals, which is affected by the "law of chemical solubility product constant" (ChSP). The present investigation focuses on the fate of heavy metals resulted from the use of primary treated sewage water for irrigating edible plant in a local sewage farm. The studied plants are maize, green beans, and alfalfa. Extensive sampling program was designed to collect both irrigated water and plant samples every two weeks. The plant samples were partitioned into roots, stems, and leaves, as well as the grains of maize and been plants. The physical and chemical characteristics of irrigated water were determined. Level of heavy metals in sewage water and all plant samples was determined. It was found that the availability of metals to plant is, generally, governed by the law of ChSP constant. In present study, the pH of both irrigated water and the soil were within the slight alkaline medium which restricted the solubility of metals. Thus, negative impact on the accumulation of metals by the irrigated plants was detected. The level of metals in all the studied plant parts was within the permissible limits according to the WHO, FAO and the Egyptian regulations. This is mainly attributed to the limited solubility of metals at the slight alkaline medium according to the law ChSP constant. It was thus concluded that the availability of metals from both irrigated waters and soils were greatly restricted and controlled by the pH value. This explains the limited accumulation of metals by all studied plants. However, log-term irrigation with sewage will certainly result in a dramatic accumulation of metals by both soil and plants. It was recommended to restrict the reuse of disinfected tertiary treated water for irrigating vegetable plants according to the local regulations.

Keywords: Heavy metals accumulation by plants, Low of chemical solubility product, Sewage irrigation, Vegetable plants, Alkaline sewage water.

Introduction

There is a widespread international concern over the lack of food in the developing countries, due to deficiency of water for irrigation and/or fertile land for cultivation. Egypt; as a developing country; suffers from both: available water and fertile land for cultivating the vast desert area that represents about 95% of the land without almost any cultivation [1, 2]. One additional problem is the continuous high rate of population that may reach more than 120 million by 2025 with limited cultivated land [3]. The major water resource in Egypt is the Nile River. Egypt consumes about 86% of the water resources for irrigation [4, 5]. Meanwhile, the sandy nature of the desert consumes large volume of water if it is irrigated [6]. Such sandy soil usually suffers from lack of fertility, micro-and macro-nutrient elements as well as water holding capacity[5]. Presently, Egypt suffers a sharp shortage of water for irrigation [7]. This fact might be more aggravated in the very near future as a result of constructing Al Nahda Dam of Ethiopia beside the possible drastic climate changes [8]. The reuse of treated wastewater as supplementary water resources for irrigation is becoming widespread in arid and semiarid countries

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due to the positive effect on sandy soi1 [9, 10].

In fact, the use of adequate treated wastewater provides a reliable alternative source for irrigation in arid and semi-arid regions [11, 12]. This water resource has been commonly used for agricultural activities due to scarcity of freshwater resources in several regions in the world [7, 11]. The main purposes are to close the gap between water demands and supply, to provide sound solution due to water scarcity and climate change, to eliminate contamination of fresh water resources, and closing the gap of achieving Millennium Development Goals [5, 6, 11].

However, the use of well treated sewage water for irrigation has an advantage of nutrient recycling. On the contrary, it has also a severe disadvantage including the uptake of heavy metals by plants, transferring the hazardous microbial deceases and contamination of groundwater [13-15].

On the other hand, it is confirmed that precipitation and co-precipitation of metal hydroxides is governed by the concentration of metal ions in solution and the pH-value. As the pH increases, the precipitation and co-precipitation of metal hydroxide increases [16]. However, certain amphoteric metals will slightly re-dissolve at high pH [16, 17].

Meanwhile, contaminating the food with heavy metals is an issue of global concern. It results; ultimately; in toxicity and diseases to both humans and animals through consumption of such food. It is worth mentioning that most heavy metals are highly toxic even at low concentrations [17]. The term heavy metals are those at atomic density greater than 4 g/cm^3, and are 5 times at least greater than the density of water [18]. In this respect, food contamination with heavy metals is one of the major environmental health challenges due to their bioaccumulation through consumption of cultivated plants irrigated with sewage water [6, 10, 19]. This may arises from the fact that sewage contains metals when it is mixed with industrial wastewater. It is also a result of the rapid industrial growth, extensive use of agricultural chemicals, and the urbanizing activities of man. All these activities have led to the dispersion of certain metals into the environment resulted; consequently; in the impaired health of Man and animals, mainly by the ingestion of food contaminated by such toxic elements [20]. Heavy metals can find their ways to plants through irrigation with contaminated water, soil, and polluted air; subsequently; accumulated along the food chain and threat both Man and animals [21-23].

The aim of the present study is to investigate the impact of sewage irrigation on selective vegetable plants in terms of heavy metals uptake. Factors affecting such uptake include level of heavy metals in the irrigated water, pH as a controlling factor on the solubility product of metals, and type of irrigated plant were considered precisely in this study. Correlation between the level of metals in the sewage water and the studied plant is a further aim. This investigation also aims to detect the highest accumulated metal and the sequence concentration of these metals in each part of plants. The permissible limits of metals accumulation by vegetable plants are also included precisely.

Materials and Methods

The present study was carried out from Jan. to Dec. 2018. The experimental investigation concentrated on a sewage farm including sampling of sewage water and three different plant samples.

Sewage Water Sampling and pH of the soil:

Monthly extensive sampling program was designed to collect samples of sewage water that was used for irrigating the sewage farm. The freshly collected sewage water samples were subjected to physical and chemical characterization as well as determination of heavy metals concentration in all samples according to APHA (2012)[24]. On the other hand, pH of the soil of this farm was also detected using portable pH meter according to APHA [24].

Plant Samples

The present study is concerning with three different plants that were irrigated by the primary treated sewage water. These three plants are maize, green beans, and alfalfa. The plant samples were collected as whole plant including leave, stem, roots, and grains. All plant parts were oven dried at 105°C for 24 hr., grinded to fine powder followed by acid digestion according to APHA (2012)[24].

Metal Determination:

Metals were determined in all the acidified water samples as well as the digested plant samples. The sewage water samples were acidified by concentrated nitric acid to below pH 2.0. Plant samples were partitioned to roots, leaves, stems and grains. All plant samples were grinded and digested using concentrated nitric acid followed by hydrogen peroxide according to procedure described by APHA [24] and recommended by other investigators [25-27]. The determined metals were Cd, Pb, Cr, Cu, Zn, Ni, Mn, and Fe. All metals were determined by Atomic Absorption and/or ICP. Na and K were determined by Flame Photometer.

Results and Discussion

Sewage Water and pH of the soil:

Physico-chemical characteristics of sewage water that was used for irrigation at Abu-Rawash sewage farm during the period from Jan. to Dec. 2018 are given in Table 1. These results showed that the pollution parameters of the given wastewater including COD, BOD_5, TSS, TKN and TP were within the primary treated wastewater according to Egyptian Guideline (Table 2) [26]. Therefore, it is allowed to be used for irrigating woody lumber trees only and it is not allowed to irrigate edible plants [26-28].

The level of heavy metals in sewage water during the period from Jan. to Oct., 2018 is given in Table 3. These results indicated that level of metals in treated sewage water was within the permissible levels according to the Egyptian code no. (501)[26], and Food and Agriculture Organization (FAO)[27]. Therefore, there is no threat concerning the heavy metals toxicity to plants. It is worth mentioning here that the industrial wastewaters were discharged along with the sewage in the sewer network systems in former times without any treatment. According to the Egyptian Manual Guidelines for Treated Waste Water Reuse in Agriculture [28], it is enforced that all kind of wastewater should be primary treated at least before discharging to the environment.

The determined pH of the soil ranged from 7.8 to 8.2 indicating the alkaline medium with an average of 8.0 (St. Dev. 0.3).

Plants irrigated by primary treated sewage water

Maize Crop:

Figure 1 represents the level of metals in different parts of Maize plants that were irrigated with primary treated sewage water. Although the wastewater contains low levels of the heavy metals, the plant samples showed distinguish values as a result of the continuous irrigation due to accumulation by the studied plants [29, 30].

The general founding is that metals were not equally accumulated by different parts of the plant. Generally, roots accumulated the highest level of all metals in correlation to the other parts of plant followed by leaf then stem. Grains contained the lowest level of heavy metals. Figure 1 illustrates the variation of selected metals as accumulated by roots, stem, leaves, and grains.

The highest accumulated metal was Zn followed by Fe, Cu and Mn, while the lowest one was Cd. The accumulated metals by this plant can be arranged according to the following descending order:

Zn > Fe > Cu > Mn > Ni > Pb > Cr > Cd

The permissible limits of heavy metals in Food additives and contaminants as a guide line were reported by FAO/WHO [31]. By correlating the level of heavy metals in the present maize plant with the permissible limits listed by the FAO/ WHO [31], it can be concluded that metals in the maize plant were still in the safe side (i.e. much lower than the permissible values). However, continuous irrigation with the primary treated sewage could certainly reach the hazardous level of heavy metals in the food.

Bean Plant:

Figure 2 illustrates the level of heavy metals in different parts of bean plants. The results showed that the studied heavy metals were accumulated mostly by roots. According to other investigators [30], these data (Fig. 2) indicated that the contents of elements in the root of bean were not only ample, but also above the requirement range for plant nutrition, while in other parts is around the normal range.

In terms of Cu, Zn and Mn content in the different parts of the plant, the higher values were detected in root and leaf while the lower values were registered in both stems and grains. Metals including Pb, Cd, Cr and Ni were much lower in the different parts of the plants than the other reported metals.

Figure 2 shows that metals in the root can be arranged according to the following decreasing order:

Fe > Mn > Zn > Cu > Ni > Pb > Ni > Cd

It is worth noticing that level of the metals in stem showed that Fe, Mn and Zn were higher than Pb, Ni, Cr and Cd. Thus, remarkable increase was exhibited in terms of the level of Zn in correlation to the other metals. Meanwhile, Zn in the leaves was associated with significant decrease in Mn. Accumulation of the nutrient elements (namely Fe, Mn, Zn, and Cu) in the different parts of the bean plant is illustrated in Fig. 2. Again,

TABLE 1. Physico-chemical characteristics of primary treated sewage water that are used for irrigation at Abu-Rawash Farm (as mg/l)

	pH	COD	BOD_5	TSS	TKN	TP
Min	7.1	133.0	63.0	30.0	25.0	3.7
Max	8.7	151.0	78.0	42.0	28.0	4.3
Average	7.8	139.7	70.0	36.1	26.3	4.0
St. Dev.	0.3	**6.0**	**5.0**	**4.3**	**1.2**	**0.2**

Min. = minimum, Max. = maximum, St. Dev. =Standard Deviations

TABLE 2. Permissible limits of water reuse for irrigation according to the Egyptian Guideline*

Parameter	Unit	1st group Primary treated wastewater	2nd group Secondary treated wastewater	3rd group Advanced treated wastewater
BOD_5	mg O_2/L	300	40	20
COD dichromate	mg O_2/L	600	80	40
TSS	mg/L	350	40	20
Oil and Grease	mg/L	Not limited	10	5
Number of cells or eggs of Nematode	Count/L	5	1	1
E.Coli count	100/ml	Not limited	1000	100
TDS	mg/L	2500	2000	2000
Na absorption ratio	%	25	20	20
Electric Conductivity	μmhos	2000~750	750~250	250

***Egyptian Guideline =** Egyptian code no. 501, 2005 for the reuse of treated wastewater in agriculture: ministry of housing, utilities and new communities [Egyptian code no. (501), 2005][26].

TABLE 3. Level of heavy metals in the irrigation water (primary treated sewage water) of Abu-Rawash WWTP during the period from Jan. to Dec. 2018 (as mg/l)

	Cu	Zn	Fe	Mn	Pb	Cd	Ni	Cr
Min	0.098	0.494	0.346	0.125	0.019	0.005	0.039	0.005
Max	0.195	1.885	0.691	0.190	0.044	0.009	0.115	0.009
Average	0.135	1.112	0.526	0.166	0.037	0.007	0.065	0.007
St. Dev.	**0.036**	**0.587**	**0.098**	**0.022**	**0.009**	**0.002**	**0.030**	**0.003**
Long term use, Maximum concentration level* (FAO, 1992)[27]	0.2	5.0	5.0	0.2	5.0	0.01	0.2	0.1
Short term use, Maximum concentration mg/l* (FAO, 1992)[27]	5.0	10.0	20.0	10.0	10.0	0.05	2.0	1.0

Min. = minimum, Max. = maximum, St. Dev. =Standard Deviations

* Water can be constantly used in all types of soil.

** Water can be used for up to 20 years in types of soft soil textures, whether neutral or alkaline.

correlation between the level of metals in both leaves and grains can be arranged according to following decreasing order:

Zn > Fe > Mn > Cu > Ni > Pb > Cd

It is noticed that the elements Fe, Mn, Pb, Cd, Ni and Cu in roots of bean were much greater than in the stems. The higher percentage of such elements was accumulated in the different parts of the bean according to the following decreasing order:

Root> Leaf> Stem> Grain

Such variation in the level of these elements reflects the external factors that affect either the activities or availability of these elements to plant [32]. It was mentioned by several investigators [33-36] that heavy metals are accumulated mostly by the root tissue of plants. Only small amounts can be transported to the other parts of plant. This explains the fact that roots in the present study accumulated the highest level of metals.

Alfalfa Plant

The illustrated data in Fig. 3 presented the measured level of heavy metals in alfalfa plant as irrigated with primary treated sewage water during the period of this investigation. These results can pronounce clearly the role of irrigation by the primary treated sewage water on the level of metals as accumulated by plants. Level of metals in both roots and leaves of the alfalfa plant can be arranged according to the following decreasing order:

Zn > Fe > Cu > Mn > Ni > Pb > Cd = Cr

Correlation between the level of metals in the stems and leave showed that the concentration values were generally within the same range particularly Mn, Cu, Cd, Ni and Cr (Fig. 3).

Discussions

Factors Affecting the Uptake of Heavy Metals by Plants:

Absorption and accumulation of heavy metals by plant tissues depend upon variable factors including: pH, moisture, temperature, organic matter, and availability of nutrients [35, 37]. In addition, heavy metal accumulation depends on plant species, while the efficiency of plants in absorbing metals is determined by irrigating-water, plant uptake and / or soil-to-plant transfer factors of the metals [32-36]. For instance, elevated lead levels in soils may decrease soil productivity, while a very low lead concentration may inhibit some vital plant processes, such as photosynthesis, mitosis, and water absorption. Similar phenomenon takes place also for cadmium [37, 38]. This leads to symptoms of toxicity, like dark green leaves, wilting of older leaves, stunted foliage, and brown short roots [37, 38]. Heavy metals are potentially toxic, resulting in chlorosis, weak plant growth, and low yield [38, 39]. They may even be accompanied by reduced nutrient uptake, disorders in plant metabolism, and a reduced ability to fix molecular nitrogen in leguminous plants [39,40].

Factors of Heavy Metals Transfer:

Metal concentrations can be calculated in the extracts of both plants and soils as dry weight. The plant concentration factor (PCF) can be calculated according to the following equation [40]:

$PCF = C_{(plant)} / C_{(soil)}$..........(John and Kakulu) [41]

Where $C_{(plant)}$ and $C_{(soil)}$ are the concentration of a given heavy metal in extracts of each one as dry weight, respectively.

Pollution load index:

The degree of soil pollution for each metal can be calculated and measured by using the pollution load index (PLI) technique that depends on the concentration of heavy metal in soil. The following modified equation is, generally, used to assess the PLI level in soils [42].

$PLI = C_{(soil)}$ in samples / $C_{(reference)}$ (Liu et al.; 2005)[42]

where $C_{(soil)}$ in Samples and $C_{(Reference)}$ in reference represent the heavy metal concentrations in the irrigated wastewater and reference soils, respectively.

Daily intake of metals by consumers: The daily intake of metals (DIM) by Man and / or animal can be determined according to the following equation:

$$DIM = \{C_{(metal)} \times C_{(factor)} \times D_{(food\ intake)}\} / B_{(average\ weight)}$$

Where $C_{(metal)}$, $C_{(factor)}$, $D_{(food\ intake)}$, and $B_{(average\ weight)}$ are presenting the heavy metal concentrations [$C_{(metal)}$] in plants as (mg/kg), conversion factor [$C_{(factor)}$], daily intake of food and /or vegetables [$D_{(food\ intake)}$], and average body weight [$B_{(average\ weight)}$], respectively. The conversion factor 0.085 was used to convert fresh green vegetable weight to dry weight, as described by Rattan et al. (2005) [43]. The average daily vegetable intakes for adults and children were considered to be 0.345 and 0.232 kg /person/ day, respectively.

Health risk index: This health risk index (HRI) for Man through the consumption of contaminated food and / or vegetables can be calculated based on the consumption of the food chain as well as the oral dose reference (RfD) for each individual metal. If the HRI <1 this means that the exposed population is safe.

HRI = DIM / RfD……(US-EPA; 2002)[44].

The present investigation revealed that the level of metals in the irrigated water are less than the permissible limit according to WHO/FAO, 1996; FAO/WHO, 2001[27, 31]. It is important to notice that the average pH of the irrigating water is 7.8 (i.e. slight alkaline) with a minimum of 7.1 and maximum 8.7. Meanwhile, the pH of the irrigated soil ranged from 7.8 to 8.2, with an average of 8.0. Thus, it can be concluded that the irrigated water and soil both are within the slightly alkaline range.

On the other hand, it is well documented that the relationship of the metal solubility product is governed by the following equation according to Feitknecht and Schindler [17].

(M^{+2}) $(OH)_2$ =====K_{sp} (solubility constant)..................Feitknecht and Schindler [17].

Such solubility product constants for metals have been already published [17]. Nevertheless, the solubility products provide an important general guide to residual metals concentration that can be expected in practice as a result of precipitates aging, incomplete solid separation, or co-precipitation and adsorption effects in wastewater [42, 43, 45].

Due to the fact that the irrigated water and soil were both in the slight alkaline medium, in the present study, thus the metals were in the range between slightly insoluble and / or precipitated form according to their recorded pH values.[17]. Therefore, it can be concluded that the availability of metals from both irrigated water and soil was greatly restricted and controlled by the pH. This explains the limited accumulation of metals by all the studied plants.

Conclusions and Recommendation

Contaminated food is one of the main sources of exposure and / or accumulated of heavy metals by Man and animals. An increase in dietary heavy metal intake may contribute to the development of various disorders in Man. It is, therefore, necessary to monitor the levels of such metals in food chain and in the body. Generally, long-term accumulation of heavy metals in soils results in contamination of food crops. Several studies proved that heavy-metal contaminated food crops, fruits, and vegetables can contain levels higher than the recommended tolerable values proposed by the Egyptian Code No. (501), USEPA, FAO, and WHO [26, 27, 31, 44]. Foodstuffs in some countries have been found to contribute to the body's burden of heavy metals, which is a matter of public health concern [45].

The characteristics of sewage in this study achieved the permissible limits of primary treated wastewater [12]. However, this treated sewage water can be used for irrigating lumber woody trees only [45]. This pronounces that the present wastewater should not be used by all means for irrigating edible and / or vegetable plants. Although the level of metals in this primary treated sewage was within the permissible limits, however, accumulation of these metals in both soil and plants is still of great concern due to their diverse impact to public health. Nevertheless, the availability of metals in both irrigating water and soil is; generally; governed by the pH value according to the chemical solubility product constant (Ksp). In the present investigation, the pH values of both irrigating water and soil were within the slight alkaline range which is characterized by a negative impact on the accumulation of metals by the irrigated plants. Finally, it is strongly recommended to further treat this given sewage water up to the tertiary stage for safe reuse.

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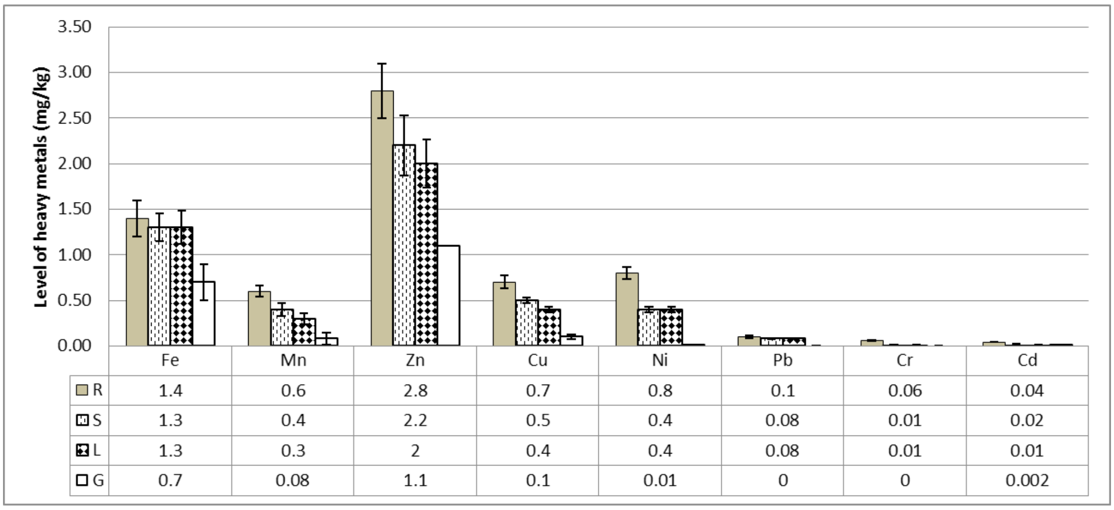
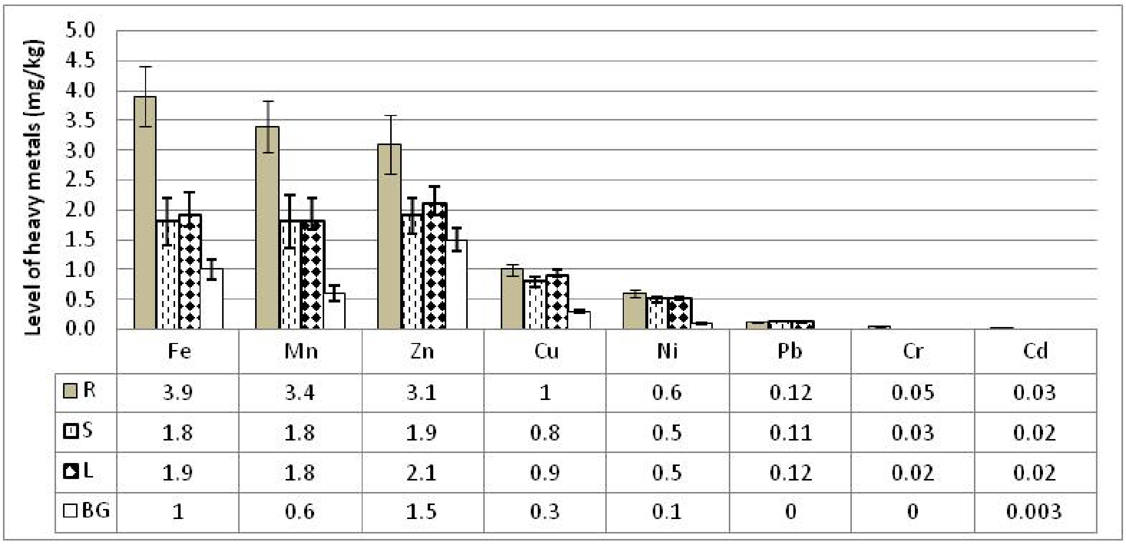


	Fe	Mn	Zn	Cu	Ni	Pb	Cr	Cd
R	1.4	0.6	2.8	0.7	0.8	0.1	0.06	0.04
S	1.3	0.4	2.2	0.5	0.4	0.08	0.01	0.02
L	1.3	0.3	2	0.4	0.4	0.08	0.01	0.01
G	0.7	0.08	1.1	0.1	0.01	0	0	0.002

R = roots, S = stems, L = leaves, G = grains

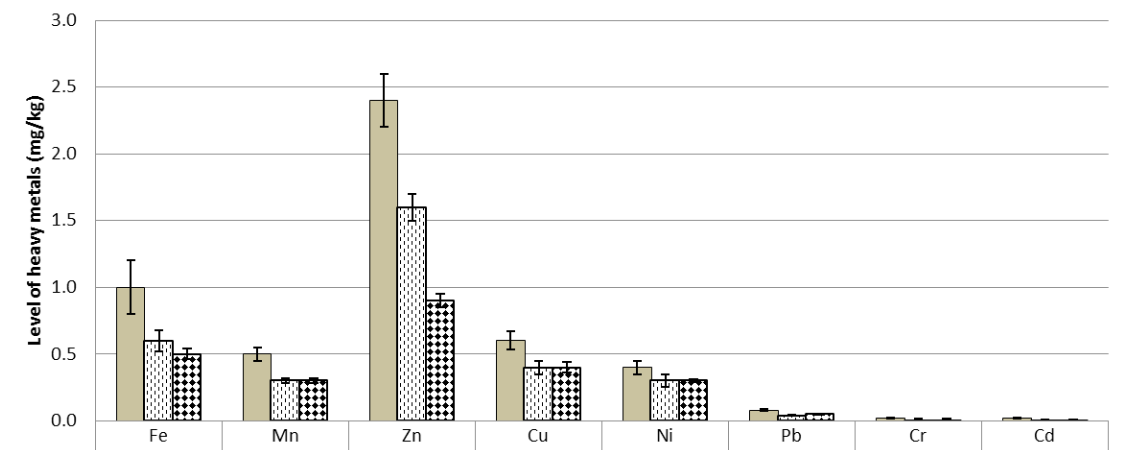
Fig. 1. Level of heavy metals (mg/kg dry weight) in different parts of Maize crop



	Fe	Mn	Zn	Cu	Ni	Pb	Cr	Cd
R	3.9	3.4	3.1	1	0.6	0.12	0.05	0.03
S	1.8	1.8	1.9	0.8	0.5	0.11	0.03	0.02
L	1.9	1.8	2.1	0.9	0.5	0.12	0.02	0.02
BG	1	0.6	1.5	0.3	0.1	0	0	0.003

R = roots, S = stems, L = leaves, BG = been grains

Fig. 2. The level of nutrient metals (mg/kg dry weight) in the different parts of bean plant



	Fe	Mn	Zn	Cu	Ni	Pb	Cr	Cd
R	1	0.5	2.4	0.6	0.4	0.08	0.02	0.02
S	0.6	0.3	1.6	0.4	0.3	0.04	0.01	0.01
L	0.5	0.3	0.9	0.4	0.3	0.05	0.01	0.01

R = roots, S = stems, L = leaves

Fig. 3. The level of heavy metals (mg/kg dry weight) in the different parts of Alfalfa plant.

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