

*Original Research*

# Estimation and Bio-Availability of Toxic Metals between Soils and Plants

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## Abstract

Heavy metals contamination of soil is one of the most alarming concerns in the debate about food security and food safety all over the world because it determines the possible composition of food and feeds at the root level of the food chain. Simultaneously, plants are important components of the ecosystem as they transfer elements from abiotic and biotic environments. The primary sources of elements from the environment to plants are air, water, and soil. The aim of this study was to determine the accumulation levels of trace toxic heavy metals in soils and plant samples in the garden of the Al-Nadwa-Riyadh area. Lead and cadmium were measured in the soil and plants by graphite atomic absorption spectrometry, while arsenic and mercury were measured using hydride generation atomic absorption spectrometry. Plant samples were digested by 8 ml of nitric acid followed by 2 ml hydrogen peroxide, while soil samples were digested by 6 ml concentrated nitric acid followed by 2 ml hydrofluoric acid and 2 ml hydrogen peroxide. In soil samples, results presented here showed that levels of lead were within the set of all standards, while cadmium exceeds the limits of FAO and EC standards. Arsenic was found to be above the FAO standard but within the set of all other standards. On the contrary, mercury was investigated far above all the set standards. All levels of the heavy metals in all plant samples were below the maximum permissible limit standard values of FAO/WHO, except mercury. The results demonstrated that mean content of Hg uptake by the plants was higher than the contents of each trace metals under test.

**Keywords:** heavy metals, plant, soil, spectroscopy

## Introduction

Soil and land contamination by heavy metals has become a serious environmental concern due to its potential adverse ecological effects. Although heavy

metals occur naturally at low concentrations in soils, they are considered soil contaminants due to their widespread occurrence, as well as their acute and chronic toxicity. The serious effects of heavy metals on soil biochemical properties are well documented [1].

Soil properties, i.e., mud content, organic substances, and pH, mainly affect organic and biochemical properties [2]. Soils contaminated by heavy metals, such as Ni, Zn, Cd, Cu, and Pb have dramatically increased during the

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last decades ago due to the use of agricultural fertilizers and pesticides, municipal waste, mining, traffic, smelting, manufacturing, emissions, and industrial effluents [3]. However, some risk element, like arsenic (As), cadmium (Cd), lead (Pb), selenium (Se), and methylated forms of mercury (Hg) are considered one of the major sources of soil pollution [4]. These metals are considered not essential for plant growth because they do not perform any known physiological function in plants. Moreover, they are also reported to have no known biological importance in human biochemical or physiological functions [5]. Their consumption even at very low concentrations can be toxic to humans.

Other metals such as calcium (Ca), cobalt (Co), magnesium (Mg), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), and zinc (Zn) are essential elements required for normal growth and metabolism of plants, and have also been reported to be of biological importance to human beings to maintain their optimal life activities. However, these elements can easily lead to poisoning when their concentrations rise above allowed limits or optimal values [6-9].

Accordingly, when concentration of heavy metals becomes more than standard or optimum levels in soil, they cause toxic effects in soil microorganisms, resulting in a change of population size, diversity, and overall activity of the soil microbial communities [10]. This indicates that heavy metal concentration in soil plays an important role in controlling metal bioavailability to plants. Ultimately, increasing heavy metal contents in the soil also increases the uptake of heavy metals by plants depending upon soil type, plant growth stages, and plant species [11].

For example, due to higher Pb concentrations in soil, some fundamental physiological activities of soil are reduced, which could affect plant quality, reduction of cell activities, and inhibition of plant growth, water absorption, and photosynthesis. Meanwhile, very low concentrations of lead (Pb) in soil could lead toxic symptoms on dark green leaves, wilting of older leaves, brown short leaves, stunted foliage, and brown short roots [12-13].

Ingestion of vegetables and food commodities irrigated with waste or improperly treated water, or grown in soils contaminated with heavy metals present possible health risks to humans and wildlife. The uptake of heavy toxic metals from soils by plants at high concentrations leads to subsequent accumulation along the food chain and may result in a greater health risk [14]. Some important supplements in the human body are influenced by consumption of food contaminated with heavy metals, causing decreased immunity, intrauterine growth retardation, disabilities associated with malnutrition, and a high prevalence of upper gastrointestinal cancer rates [15]. The risk of transference of heavy metals from soil to plants and from plants to humans should be a matter of great concern [16]. Absorption of heavy metals by plant roots from soil (one of the major routes for the entrance of heavy metals into the food chain) and the following

accumulation along the food chain is a potential threat to animal and human health, particularly crops [17].

Most studies have shown that the use of wastewater contaminated with heavy metals for irrigation over a long period of time increases the heavy metal contents of soils above the permissible limit [18]. Wastewater from the chemical industry and chemical laboratories is one of the most important sources of heavy metal contamination leading to the pollution of groundwater and agricultural soil. In recent years, factory wastewater was discharged into rivers, lakes, and coastal areas, resulting in serious pollution problems in the water environment and causing negative effects to the ecosystem and human life. This wastewater may contain numerous toxic and harmful substances in the form of heavy metals, petroleum, and chlorinated hydrocarbons, alkalis, various acids, dyes, and other chemicals such as pesticides, herbicides, and fertilizers, which change the physiochemical properties of water [19].

All these chemicals are quite harmful or even fatally poisonous to the aquatic ecosystem [20-21]. Heavy metals from mining locales may reach agricultural soils through leaching. Also, during the rainy season large quantities of tailings and waste containing heavy metals are carried by runoff to agricultural fields near mining sites, which leads to elevated levels of heavy metals in soils [22].

#### Transfer Factor (TF)

Transfer factor (TF) describes the amount of heavy metal transferred from the soil to the plant under equilibrium conditions [23-24]. Heavy metals from the soil are consumed by plant roots and then distributed in various plant tissues. Transfer of this heavy metal from soil to plant tissues is measured using the TF indicator, which measures the ratio of the concentration of a specific metal in plant tissue to the concentration of the same metal in soil – both represented by the same units. If the TF values are  $\geq 1.0$  it shows a higher uptake of metal from soil by the plant, while lower values mean less absorption of the metal from the soil, and the plant can be used for consumption [25]. This theory assumes a linear relationship between the concentrations of a certain element in the plant with that in the soil:

$$C_{\text{Plant}} = a + \text{TF } C_{\text{Soil}}$$

...where " $C_{\text{plant}}$ " and " $C_{\text{soil}}$ " are the concentrations of an element in plant and soil, respectively, and parameter "a" is zero if the element enters the plant only from the soil. This linearity does not hold for essential elements (the contents of which are under strict metabolic control), but can hold for non-essential elements and pollutants.

This paper focusses on the study of accumulation of some heavy metals (Pb, Cd, As, and Hg) in some varieties of plants in Saudi Arabia that are irrigated with treated

water in the Al-Nadwa Garden in Riyadh. Heavy metals were quantitatively determined by the atomic absorption spectroscopy (AAS) method. Selection of these metals was based upon their potential contribution in causing threats to various biotic and abiotic components of the environment [25].

## Materials and Methods

### Collecting Plant and Soil Samples

Twenty different types of ornamental plant along with their leaves and flowers were collected in acid-washed polyethylene bags according to the sampling procedures of Tony and Australian National Botanic Gardens (Table 1) [26-27]. In addition, 20 soil samples were collected in acid-washed polyethylene bags from different locations from a depth of approximately 10-30 cm under each plant and placed in plastic bottles according to the method of Zhang [28]. The plants and soils were collected randomly inside the premises of Al-Nadwa Garden.

### Plant and Soil Sample Treatments

#### *Plant Sampling*

The collected plant samples were washed two to three times with tap water, and then again washed two to three times with distilled deionized water to remove dust particles, and were dried overnight in an oven at 95°C. The dried samples were ground in an electrical grinder to make powder. The powdered plant samples were transferred to acid-washed and labeled polyethylene bags and stored until further analysis.

#### *Soil Sampling*

Collected soil samples were brought to the laboratory and mashed with the help of a pestle and mortar, and transferred to an acid-washed labeled china crucible. The crucibles along with the samples were dried in an electric oven at 105°C overnight. All the dried soil samples were passed through a fine sieve to separate the un-gradable stone residues. The sieved soil samples were ground in a grinder to make powder and stored in acid-washed polyethylene bags until further laboratory analysis.

### Digestion Methodology for Plant Samples

Correctly weighed 0.250 grams of each sample were transferred to acid-washed PTFE vessels, and 8 ml of reagent-grade nitric acid (69%) was added to each vessel, followed by 2 ml of (35%) hydrogen peroxide. All vessels were tightly closed and loaded into a Milestones Ethos One microwave digestion system

Table 1. Names of plants.

Plant Sample I.D	Name of Plant
1	Cestrum nocturnum
2	Rosa rubiginosa
3	Euonymus japonicus "Silver king"
4	Magnolia
5	Dracaena fragrans
6	Conocarpus erectus
7	Jasmine
8	Dracaena braunii
9	Ficus benjamina
10	Syngonium
11	Dieffenbachia
12	Peppermint.
13	Scindapsus
14	Dracaena fragrans
15	Sphagneticola
16	Petunia
17	Malva parviflora
18	Cordyline indivisa/australis
19	Yucca
20	Purple heart

[29-30]. The microwave digestion system was run as indicated below:

Time (t)	Temperature (°C)	Watts (energy)
15 mints.	180	1500
20 mint (hold time)	180	1500

After the run was completed, all vessels in the system were allowed to cool for 10-15 minutes. The vessels were taken out and each digested sample was transferred to 50 ml volumetric flasks. We added an appropriate volume of deionized distilled water to make the volume exactly 50 ml. Each sample was filtered through a 0.45 µ PTFE filter and stored in properly labeled polyethylene bottles and refrigerated at 4°C until further analysis.

### Digestion Methodology for the Soil Samples

Exactly 0.250 grams of soil were weighed from each soil sample and placed in PTFE vessels. Then we added 6 ml reagent-grade concentrated nitric acid (69%) followed by 2 ml of (48%) hydrofluoric acid and 2 ml of (35%) hydrogen peroxide and waited for 10-15 mins to complete the reaction. All vessels were tightly closed

Table 2. Standard operating parameters of the elements analyzed in plants.

Parameters	Pb	Cd	As	Hg
Wavelength (m)	283.3	228.8	197.2	253.7
Slit Width (nm)	0.5	0.5	0.5	0.5
Lamp Current (mA)	10	4	10	4
Sensitivity (mg/kg) At 0.2 Abs	27	1.00	50	70
Detection Limit (mg/kg)	0.002	0.00006	0.0028	0.002
Quantification Limit (mg/kg)	0.006	0.00018	0.0084	0.006
Optimum Working Range (mg/kg)	0.006-0.03	0.00018-0.001	0.0084-0.1	0.006-0.03
Instrument	GT-AAS	GT-AAS	HG-AAS	HG-AAS

Table 3. Standard operating parameters of the elements analyzed in soils.

Parameters	Pb	Cd	As	Hg
Wavelength (m)	283.3	228.8	197.2	253.7
Slit Width (nm)	0.5	0.5	0.5	0.5
Lamp Current (mA)	10	4	10	4
Sensitivity (mg/kg) At 0.2 Abs	27	1.00	50	70
Detection Limit (mg/kg)	0.5	0.047	0.027	2.7
Quantification Limit (mg/kg)	1.6	0.144	0.082	8.3
Optimum Working Range (mg/kg)	1.6-2.5	0.144-0.600	0.08-0.25	8.3-25
Instrument	GTAAS	GTAAS	HGAAS	HGAAS

and loaded into the microwave digestion system [31-32], and the system was run as indicated previously. After the run was completed, the vessels were taken out and each digested sample was transferred to 50 ml volumetric flasks, and the volume of each sample was adjusted accurately up to 50 ml with deionized distilled water. Now each sample was filtered through a 0.45  $\mu$  PTFE filter and stored in properly labeled polyethylene bottles until further analysis.

#### Instrumentation

We used a high-performance Ethos One microwave digestion system, a 240FS AA atomic absorption spectrometer from Agilent Technologies with (Graphite Furnace) GTA 120 “æ” “PSD” 120, a programmable sample dispenser, and argon carrier gas. The operating conditions during the analysis of heavy metals are listed in Tables 2-3 for plant and soil, respectively. Clear solutions of the digested samples were analyzed by graphite atomic absorption spectrometry (GTAAS) for Pb and Cd using argon gas, while As and Hg were analyzed by the hydride generation atomic absorption spectrometry (HG – AAS, AAS 240FS) method using flame atomic absorption spectrometry (FAAS) with air-acetylene (model: AAS 240FS), Agilent Technologies Company, USA, by the

standard calibration technique. All measurements were run in triplicate for the samples and standard solutions and the results reported as the main  $\pm$  standard deviation. All the results were statistically significant at  $P < 0.05$ .

#### Statistical Analysis

The data were analyzed using Package for Social Science (SPSS) v. 20 statistical software (SPSS Inc., Chicago, IL, USA) after data were normalized by log transformation. Descriptive statistical parameters such as mean and standard deviation (SD) were used to describe the heavy metal concentration in soils and plants, and differences were considered statistically significant with  $p$  value  $< 0.05$ . One sample test, Sig. (2-tailed) was used to determine the difference of the heavy metals concentrations in soils and plants at a significance level of  $p < 0.05$ .

#### Results and Discussion

Heavy metals may enter the human body through inhalation of polluted dust, contaminated soil used for irrigation, and food plants grown on metal-contaminated

Table 4. Statistical description of the experimental results of soil samples.

Soil sample number	Mean conc. of Pb in mg/kg $\pm$ S.D	Mean conc. of Cd in mg/kg $\pm$ S.D	Mean conc. of As in mg/kg $\pm$ S.D	Mean conc. of Hg in mg/kg $\pm$ S.D
1	1.96 $\pm$ 0.0004	0.430 $\pm$ 0.0010	0.237 $\pm$ 0.0015	15.066 $\pm$ 0.0004
2	1.92 $\pm$ 0.0002	0.422 $\pm$ 0.0015	0.2160 $\pm$ 0.0031	12.380 $\pm$ 0.0003
3	2.10 $\pm$ 0.0002	0.438 $\pm$ 0.0062	0.2183 $\pm$ 0.0021	11.527 $\pm$ 0.0003
4	1.95 $\pm$ 0.0002	0.437 $\pm$ 0.0015	0.2161 $\pm$ 0.0021	10.719 $\pm$ 0.0011
5	1.92 $\pm$ 0.0002	0.465 $\pm$ 0.0015	0.1995 $\pm$ 0.0010	10.485 $\pm$ 0.0043
6	2.20 $\pm$ 0.0001	0.460 $\pm$ 0.0010	0.2183 $\pm$ 0.0025	9.726 $\pm$ 0.0003
7	1.60 $\pm$ 0.0002	0.462 $\pm$ 0.0015	0.2086 $\pm$ 0.0020	10.331 $\pm$ 0.0002
8	1.60 $\pm$ 0.0001	0.473 $\pm$ 0.0015	0.2134 $\pm$ 0.0021	12.077 $\pm$ 0.0005
9	1.68 $\pm$ 0.0223	0.498 $\pm$ 0.0020	0.2172 $\pm$ 0.0020	11.254 $\pm$ 0.0004
10	1.79 $\pm$ 0.0002	0.494 $\pm$ 0.0020	0.2090 $\pm$ 0.0020	11.149 $\pm$ 0.0003
11	1.64 $\pm$ 0.0015	0.507 $\pm$ 0.0015	0.1951 $\pm$ 0.0010	9.901 $\pm$ 0.0005
12	1.60 $\pm$ 0.0001	0.501 $\pm$ 0.0015	0.1951 $\pm$ 0.0012	10.425 $\pm$ 0.0004
13	1.61 $\pm$ 0.0012	0.515 $\pm$ 0.0015	0.1971 $\pm$ 0.0020	10.984 $\pm$ 0.0003
14	1.60 $\pm$ 0.0002	0.508 $\pm$ 0.0015	0.1892 $\pm$ 0.0015	11.112 $\pm$ 0.0004
15	* not detected	0.509 $\pm$ 0.0021	0.2120 $\pm$ 0.0015	10.885 $\pm$ 0.0003
16	* not detected	0.519 $\pm$ 0.0015	0.1830 $\pm$ 0.0010	15.151 $\pm$ 0.0005
17	1.78 $\pm$ 0.0002	0.516 $\pm$ 0.0025	0.1971 $\pm$ 0.0021	12.929 $\pm$ 0.0004
18	1.97 $\pm$ 0.0003	0.532 $\pm$ 0.0010	0.2261 $\pm$ 0.0010	13.968 $\pm$ 0.0009
19	1.66 $\pm$ 0.0001	0.553 $\pm$ 0.0015	0.2102 $\pm$ 0.0010	13.100 $\pm$ 0.0007
20	* not detected	0.542 $\pm$ 0.0010	0.2331 $\pm$ 0.0015	12.099 $\pm$ 0.0005
Min.	1.60	0.422	0.1830	9.726
Max.	2.20	0.553	0.2370	15.151
Mean	1.76	0.49	0.21	11.76
STD	0.0015	0.0018	0.0017	0.0007
Mean $\pm$ STD	1.76 $\pm$ 0.0015	0.49 $\pm$ 0.0018	0.21 $\pm$ 0.0017	11.76 $\pm$ 0.0007

\*N/D (not detected)

soil [33]. Despite the poor bioavailability of heavy metals in soil, the plants may have a high ability to accumulate them in their different parts [34]. So, analyses of wild edible plants are important to identify and measure the

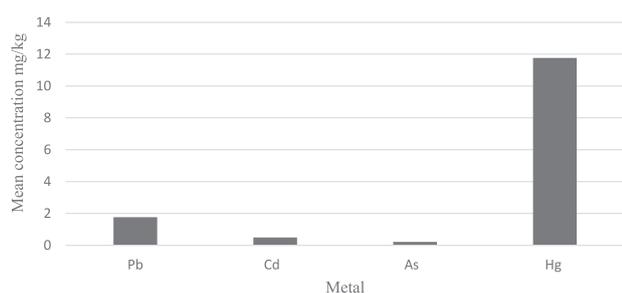


Fig. 1. Mean concentrations of metals in soils.

level of toxic metals. The present study was carried out to evaluate the level of heavy metal contamination in the various types of soil and plants in the garden of Al-Nadwa. In all soil samples, the results showed the presence of Cd, As, and Hg, but Pb was not detected at the sites (15, 16, 22).

The results of heavy metal concentrations in soils are given in Table 4 and Fig. 1. Lead as a soil contaminant is a widespread issue; it accumulates with age in bones, the aorta, kidneys, liver, and spleen. The probability of lead (Pb) entrance in the human body by food is 65%, by water 20%, and by air 15%.

The calculated range of the concentrations of Pb in soils was 1.6-2.2 mg/kg, except samples 15, 16, and 20, which have fallen below the detection limit of the instrument. All were within the set standards of FAO/WHO and Ling-Zhi [35-36], Austria, Germany,

Table 5. Permissible limits of metals in soil by different standards.

Standards/Guidelines	Pb mg/kg	Cd mg/kg	As mg/kg	Hg mg/kg
FAO/WHO	90-400	-	-	1.0
EC	0.30	0.003	20	-
United States	50-300	1.6	14	0.5
Poland	70-150	1-3	30	5
Germany	100	1.5-3	20	2
Austria	100	5	50	5

Poland, the United States, and the European Council for European communities standards (Table 5) [26, 28].

Concentrations of Cd in soils (0.422-0.553 mg/kg) were far above the FAO/WHO and EC standards and within the set standards of Austria, Germany, Poland, and the USA, while the concentrations of As in soils (0.183-2.37 mg/kg) were far above the FAO/WHO standard and within the set standards of Austria, Germany, Poland, the USA, and EC (Table 5). In contrast, the concentrations of Hg analyzed in soils were by far above the FAO/WHO, Austria, Germany, Poland, USA, and EC set standards (Table 5). The order of the metals concentrations in soils (mean±STD) is: Hg (11.76±0.0007) > Pb (1.76±0.0015) > Cd (0.49±0.0018) > As (0.21±0.0017).

The reason for this extremity in values might be due to the addition of civic wastes and effluents as the sewage of the factories and universities near a garden.

Table 6. Statistical description of the experimental results of plant samples.

Plant sample number	Mean conc. of Pb in mg/kg ±S.D	Mean conc. of Cd in mg/kg ±S.D	Mean conc. of As in mg/kg ±S.D	Mean conc. of Hg in mg/kg ±S.D
1	0.006±0.0056	0.0006±0.0105	0.01±0.0026	2.51±0.0002
2	0.100±0.0013	0.0005±0.0033	0.01±0.0009	2.44±0.0003
3	0.007±0.0005	0.0004±0.0008	0.01±0.002	2.57±0.0003
4	0.006±0.0097	0.0006±0.0038	0.02±0.0160	3.19±0.0010
5	0.006±0.0024	0.0010±0.0024	0.01±0.0044	3.04±0.0010
6	0.006±0.0023	0.0006±0.0041	0.01±0.0063	2.94±0.0003
7	* not detected	0.0006±0.0022	0.02±0.0030	3.13±0.0008
8	* not detected	0.0006±0.0034	0.01±0.0024	2.66±0.0006
9	0.007±0.0011	0.0006±0.0019	0.03±0.0019	3.55±0.0001
10	0.007±0.0025	0.0008±0.0018	0.01±0.0020	2.43±0.0004
11	0.0110±0.0010	0.0007±0.0016	0.02±0.0012	3.12±0.0005
12	* not detected	0.0006±0.0004	0.02±0.0028	2.62±0.0003
13	0.007±0.0031	0.0005±0.0016	0.01±0.0022	2.53±0.0020
14	0.007±0.0053	0.0005±0.0016	0.01±0.002	3.09±0.0002
15	0.01±0.0007	0.0008±0.0020	0.02±0.0020	2.66±0.0001
16	* not detected	0.0005±0.0044	0.01±0.0023	2.23±0.0005
17	0.008±0.0013	0.0008±0.0045	0.03±0.0016	2.51±0.0008
18	0.01±0.0044	0.0005±0.0073	* not detected	* not detected
19	0.010±0.0580	0.0008±0.0011	0.02±0.0030	3.22±0.0001
20	0.01±0.0150	0.0008±0.0074	0.02±0.0024	3.76±0.0033
Min.	0.006	0.0004	0.008	2.23
Max.	0.100	0.001	0.027	3.76
Mean	0.012	0.0006	0.03	2.7
STD	0.006	0.003	0.003	0.001
Mean±STD	0.012±0.01	0.0006±0.003	0.015±0.003	2.7±0.001

\*ND (Not Detected)

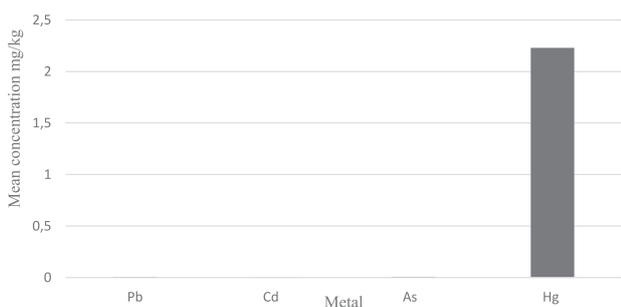


Fig. 2. Mean concentrations of metals in plants.

This agrees with the studies reporting that the level of heavy metals increasing in the soils due to the discharge of laboratories and industrial effluents and civic pollution of various kinds [37]. This is, in turn, deteriorating the soil and plant quality, making it unsuitable for both aquatic and human life. Mercury could be present in the soil in different forms. It dissolves as a free ion or soluble complex and is nonspecifically adsorbed by restricting fundamentally due to electrostatic forces, chelating potential, and precipitated as sulphides, carbonates, hydroxides, and phosphate. The results of this study showed that the averaged Hg concentration (11.76 mg/kg) was higher than its background (0.065 mg/kg) [38].

The results demonstrated that all the trace metals under examination were seen to be absorbed by all plants, but Pb, As, and Hg were not detected in samples (7, 8, 12, and 16), 18 and 18, respectively (Table 6, Fig. 2). Mercury was absorbed by plants as the sequence purple heart > (3.76±0.0033) > Ficus Benjamina (3.55±0.0001) > Magnolia (3.19±0.0010) > Jasmine (3.13±0.0008) > Dieffenbachia (3.12±0.0005), while the second was Pb, third was As, and fourth was Cd as the following (0.01±0.01) absorbed by Rosa Rubiginosa, (0.01±0.01) absorbed by Rosa Rubiginosa, (0.100±0.0013) absorbed by Rosa Rubiginosa, (0.03±0.0019) absorbed by Ficus Benjamina, and (0.0010±0.0024) absorbed by Dracaena Fragrans (Table 6, Fig. 2).

The results showed that in the soil samples the mean concentrations (mg/kg) of Pb, Cd, As, and Hg are, respectively: 1.76±0.0015, 0.49±0.0018, 0.21±0.0017, and 11.76±0.0007. The average concentrations of plants from (1-20) are, respectively: 0.012±0.01, 0.0006±0.003,

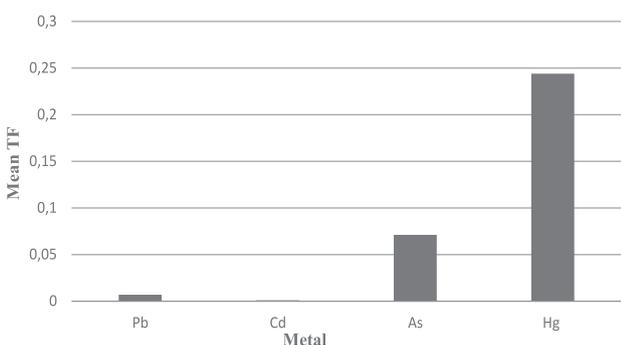


Fig. 3. Mean concentrations of TF plant to soil.

Table 7. Translocation factor of metals from plant to soil.

Plant sample number	Lead	Cadmium	Arsenic	Mercury
1	0.003	0.001	0.042	0.167
2	0.052	0.001	0.032	0.197
3	0.003	0.001	0.041	0.223
4	0.003	0.001	0.093	0.297
5	0.003	0.002	0.065	0.290
6	0.003	0.001	0.050	0.302
7	0.003	0.001	0.101	0.303
8	0.003	0.001	0.052	0.220
9	0.004	0.001	0.115	0.315
10	0.004	0.002	0.067	0.218
11	0.007	0.001	0.103	0.316
12	0.003	0.001	0.077	0.251
13	0.004	0.001	0.051	0.230
14	0.004	0.001	0.048	0.278
15	0.006	0.002	0.094	0.244
16	0.003	0.001	0.060	0.147
17	0.004	0.002	0.137	0.194
18	0.005	0.001	0.027	0.127
19	0.006	0.001	0.086	0.245
20	0.011	0.001	0.077	0.311
Average TF	0.007	0.001	0.071	0.244

0.015±0.003, and 2.7±0.001 for Pb, Cd, As, and Hg.

A study by Brian divided some metals into less, medium, and high potential to be accumulated in plants: As> Pb > Hg are the metals showing medium accumulation with TF = 0.01–1.00, the current study showed that potential to be accumulated in plants: Hg > As > Pb are the metals showed medium accumulation with TF = 0.007–0.241 (Table 7) [39]. In the case of Cd, according to Brian, it was one of the elements intensively accumulated in plant bodies with TF = 1.00–10.00 (Table 7), which does not agree with the current study where TF of Cd were 0.001, which may due to Cd being absorbed by the plants, then accumulating in different tissues (Table 6, Fig. 3).

In our present study, As, which showed medium content in soil under examination, recorded low amounts in plants. This might be due to a higher pH, and the accessibility of As in solution form is less, which hinders the soil-plant transfer. All mean content of the heavy metals in all plant samples fall below the maximum permissible limit standard values except Hg, (Table 8). This study showed that the mean contents of Hg (2.7±0.001) absorbed by the plants are higher than the contents of each trace metal under test.

Table 8. Permissible limit values of the metals in plants by different standards.

	Type of plant	Pb (mg/kg)	Cd (mg/kg)	As (mg/kg)	Hg (mg/kg)
FAO/WHO, 1999	leafy vegetables	0.20	0.10	0.10	0.030
FAO/WHO, 2001	vegetables	0.30	0.20	0.43	0.03

Cadmium is absorbed by all the plants almost equally by the 12 plants ( $0.0006 \pm 0.004 - 0.0008 \pm 0.003$ ), while Pb was the second metal absorbed by the five vegetables ( $0.0007 \pm 0.0025$ ). In the current study, TF of metals from soil to plant was (0.007, 0.001, 0.071 and 0.244) for Pb, Cd, As and Hg, respectively (Table 8, Fig. 3). That was to say with a sequence of decreasing TF values: Hg As Pb Cd.

The higher the value of transfer factor, the more element would be accumulated by plants. Mercury is the element with the highest TF values, which agrees with Yang, who reported a sequence of decreasing TF values as: Ni>Hg>Zn>Pb>Cr=Cd>Cu>Mn. Hg can be generalized for plants in the Rudna mine area [40]. The heavy metals Hg and As have greater soil-plant transfer rates than Pb and Cd (Table 7). The plants under test accumulate Hg in the following decreasing order: 0.316>0.315>0.311>0.303>0.302>0.297>0.29>0.278>0.251>0.245>0.244>0.23>0.223>0.22>0.218>0.197>0.194>0.167>0.147>0.127.

All the plants that can accumulate arsenic, cadmium, and lead are the least to be accumulated by all the plants. Gaile and Klavins stated that the lowest values of transfer factor for some plants grown in soils with the highest contamination levels of trace metals and with the addition of a solution of humic substances by that affirming intensity of metal sorption processes in soil connected with the presence of organic matter [41]. Plants

and their soil samples do not accumulate metals equally. The accumulation and distribution were dependent on environmental factors [42].

Various studies explained that the absorbable availabilities of metals are not the only influencing factors for the bio-transfer of trace metals but also the plant species tendency to uptake a certain element from the soil [43-44].

### Plant Correlation Analysis

Correlation analysis was carried out for trace heavy metals concentrations and plant associations in order to understand the significance ( $p = 0.05$ ,  $p < 0.05$ ) of the association between metals and plants. The Pearson correlation coefficient matrix for trace heavy metals (Pb, Cd, AS, and Hg) and plant samples is presented in Table 9. The analysis of the interrelationship between the heavy metals and plants offers remarkable information on free ion availability. The computed statistical results showed that Hg has significant positive correlation with As ( $r = 0.461$ ).

Mercury has moderate insignificant positive correlation with Cd ( $r = 0.341$ ) and insignificant negative correlation with Pb ( $r = -0.091$ ). The negative correlation values show that as one variable increases in value, the second decreases. 50% of the metals are positively correlated (except for Pb–Cd, Pb–As, and Pb–Hg).

Table 9. Pearson correlations of trace heavy metals with vegetables.

		Pb	Cd	As	Hg
Pb	Pearson Correlation	1	0.191	0.156	0.091
	Sig. (2-tailed)		0.421	0.511	0.702
	N	20	20	20	20
Cd	Pearson Correlation	0.191	1	0.347	0.341
	Sig. (2-tailed)	0.421		0.133	0.142
	N	20	20	20	20
As	Pearson Correlation	0.156	0.347	1	0.461*
	Sig. (2-tailed)	0.511	0.133		0.041
	N	20	20	20	20
Hg	Pearson Correlation	0.091	0.341	0.461*	1
	Sig. (2-tailed)	0.702	0.142	0.041	
	N	20	20	20	20

\* Correlation is significant at the 0.05 level (2-tailed).

The positive linear relationship of Cd–As and Cd–Hg) was weak. Just Hg and As are respectably moderately associated with each other because both may have the normal sources or might be affected by the same agents. The basic sources of such contamination could either be the cultivating locals irrigated with dirtied water or atmospheric deposition of these metals because of vehicle contamination or sources of soil formation.

### Conclusion

Concentrations of trace heavy metals in our studied soil samples show that Pb was within the set of all standards, while cadmium exceeded that of FAO/WHO and EC, but fell within all other standards (Ling-Zhi, Austria, Germany, Poland, USA). Arsenic was by far the within FAO/WHO limits, but within the set of all other standards. On the contrary, mercury was far above all the set standards (Table 6).

The mean content of all heavy metals in all our tested plant samples was below the maximum permissible standard values except for Hg, which was above the standard limits set by FAO/WHO (Table 5). The detection of this toxic metal in our tested plant samples clearly indicates a persistent exposure of plants to soil contaminated with abnormally high concentrations of Hg. Consumption of such contaminated edible plants for prolonged durations causes the accumulation of this highly neurotoxic substance in the human body, posing a serious health hazard to humans as well as animals.

Based on the results of this study, it is highly recommended that concerned authorities should carry out routine screening of soil as well as crops for the presence of toxic heavy metals.

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### Conflict of Interest

The authors declare no conflict of interest.

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