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RESEARCH PAPER

Determination of trace metals in vegetables using ICP-MS

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A B S T R A C T:

The aim of this research was to evaluate the total content of heavy metals in selected and frequently used vegetables. Ten samples of the most common diet vegetables (chard, celery, garden cress, spinach, Egyptian leek, wild mint, spring onion, arum, mallow, sunflower) were collected from the local markets in Erbil, in the Kurdistan region of Iraq. The heavy metals were extracted from vegetable samples by microwave-assisted acid digestion utilizing nitric acid/hydrogen peroxide, followed by inductively coupled plasma-mass spectrometry (ICP-MS) to determine the concentrations of As, Cd, Cr, Cu and Pb in the samples. The concentration ranges of heavy metals found for the ten types of edible vegetables investigated are as follows (in µg g-1): As, 0.198-0.436; Cd, <LOD-0.396; Cr, 1.653-11.915; Cu, 3.956-17.782 and Pb, 0.244-1.323. The method was validated for total As, Cd, Cr, Cu and Pb extraction by analysing a certified reference material of GBW10015-spinach. From health point of view estimated daily intake and carcinogenic risks of heavy metals were evaluated. Estimated daily intake values of these heavy metals were found to be lower than the maximum tolerable daily intake. This study also shows that the carcinogenic risk for As, Cd, Cr and Pb exceeded the acceptable level. The results of this work recommend that consumers should be more cautious about levels of heavy metals (especially As, Cd, Cr and Pb) in the analysed vegetable samples in order to make sure the vegetable safety for consumers in Erbil city- the Kurdistan region of Iraq.

KEY WORDS: Heavy metals, edible vegetables, inductively coupled plasma-mass spectrometry, estimated daily intake, carcinogenic risk.
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1.INTRODUCTION:

Human body requires a number of minerals that can be obtained from plants for growth and activities, because plants absorb and accumulate minerals from environment which requires for its growth. Metals can be accumulated in plants from the environment (Gajalakshmi et al., 2012). Different minerals are reported, traces of As, Cd, Cr, Cu and pb have been detected in plants and food stuffs (Rai et al., 2019). is a species very closely allied to *F. tulipifolia* and *F. armena*. Their The term ‘heavy metal’ is useful for describing a wide number of elements, which performs as group of toxicants. As a result of industrial activities, producing and accumulation of heavy metals have grown. Number of metals, such as Mn, Cu, Zn, Mo and Ni, are considered to be essential or useful micronutrients for microorganisms, plants, and animals, however tremendous contents of these metals have a negative consequence may threat environment (Gajalakshmi et al., 2012; Tahar and Keltoum, 2011).

Plants can be polluted by microbial growth or metals caused by several factors including environment, pollution, atmosphere, soil, harvesting and handling. Therefore, it is necessary to determine the concentration of these metallic elements, because consuming high levels of these elements cause toxicity. The World Health Organization urges to ensure the quality of plants and its products using appropriate techniques and applying standard measurements (Dudka and Miller, 1999; Gajalakshmi et al., 2012).

Various physical and chemical properties of soil affect the bioavailability of heavy metals to plant such as pH, organic matter content, redox

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potential, cation exchange capacity (CEC), sulphate, carbonate, hydroxide, texture of soil and clay content, taken up by root (Intawongse and Dean, 2006). In addition, the characteristics of the plant, cultivar, stage of growth, and compartment of the plant, the content may influence the absorption of heavy metals. (Habib et al., 2011; Nan et al., 2002). Transferring metals from sediments to the foodstuffs occurs through absorption of heavy metals by the plants (Gajalakshmi et al., 2012).

Bioaccessibility of metals for plant absorption can be classified into three categories: bioavailable heavy metals including As, Cd, Cu, Ni and Zn, reasonably bioavailable (Mn) or minimum bioavailable (Cr and Pb). The availability of Fe, Cu, Mn, and Zn is quite inferior in alkaline soils but in acid soils the concentration of Al and Mn would increase to poisonous levels and impact adversely on plant progress (White, 2012).

Accumulation of heavy metals through the food chain results in problems with oxidation condition of living cell, peroxidation of lipid, damaging filaments of DNA, protein expression and folding, deterioration in proteasome, protein interchanges, revolution and death of cell (Parris and Adeli, 2002; Khan et al., 2015; Cvjetko et al., 2014). Some diseases including a deterioration in impenetrable defences, delay of preventative development, defective of psycho-social conduct, impairment linked with malnutrition, and a high pervasiveness of elevated gastrointestinal cancer occur because of ingestion of food and vegetation polluted with heavy metals (Deribachew et al., 2015).

The As species can be highly toxic to human and domestic animals (Codex Alimentarius Commission, 2016). As may harm the majority of terrestrial plants (Jedynak et al., 2009). Most plant species can uptake As through the water flow and accumulate in the plants. It was estimated that the edible plant to have the As concentration with a range of 0.01 to 0.06 $\mu g\ g^{-1}$, some edible plants are able to tolerance high levels of As with average of 2 $\mu g\ g^{-1}$ (Kabata-Pendias and Mukherjee , 2007; Samantaray et al., 1998).

It is considered that Cd is a toxic industrial pollutant with expressed mobility and widely spread in nature (Valko et al., 2005). It has been reported that high levels of Cd have been found in the organs of edible plants since Cd becomes a great issue for food security (Grytsyuk et al., 2006). Cr functions as a nutritive improvement to glucose digestion for humans therefore its important for them and for animals as well because it has function in normal digestion of carbohydrates and lipids cancer (Samantaray et al., 1998). Although chromium (III) is classified as an essential element, chromium (VI) is a human carcinogen and leading to increased risk of lung cancers especially bronchogenic and nasal (Wilbur et al, 2012). The plant poisonous levels of Cr in superior part of plants were found to be as follows: 18 to 24 $\mu g\ g^{-1}$ in tobacco, 4 to 8 $\mu g\ g^{-1}$ in corn and 10 $\mu g\ g^{-1}$ in barley seedlings (Kabata-Pendias, 2011).

Although Cu is a crucial element for plant nutrient, it shows toxicity at high concentrations. Cu is involved for constituting enzymes catalyzing redox reactions, and it is necessary in photosynthetic functions (Adrees et al., 2015). The elevated quantity of reactive oxygen species (ROS)is persuaded and the photosystem in photosynthesis will be affected by excess Cu (Schutzendubel and Polle, 2002; Bouazizi et al., 2010; Quartacci et al., 2000), which leads to reduce the yield or quality of crops. The toxic effects of Cu have been investigated in different crops. If the concentration of Cu in soil is more than 300 $\mu g\ g^{-1}$ the yields of rice grain will be reduced about 50 % (Xu et al., 2006). At low concentration, Pb and Cd induce toxicity because they are not essential for human, animals and even plants. Pb has been detected in some environmental and biological samples (Guerra et al., 2012).

The purpose of this study was to determine the concentration of heavy metals in some common and different edible vegetable species and estimate its validity and suitability for human beings use according to health risk assessments.

2. MATERIALS AND METHODS

2.1 Chemicals and Reagents

Analytical pure chemicals were used in this study. Milli-Q water (18MΩcm) was used to prepare all solutions. The high purity stock solution 100 $\mu g\ mL^{-1}$ in 5 %HNO_3 obtained from CPI international (Peak performance, USA) was used to prepare standard solutions of total As, Cd, Cr, Cu and pb. Hydrogen peroxide 37% and nitric acid 70% were purchased from Merck. Spinach

GBW10015 certified reference material (CRM) (Institute of Geophysical and Geochemical Exploration, Langfang, China) was supplied by LGC standards (Middlesex, UK).

2.2 Instrumentation

An Agilent 7500 instrument (USA) ICP-MS was used to measure total elements in extracts of vegetable samples. The employed working parameters are shown in Table 1. Possible interferences were eliminated using collision cell technology. Final concentration of 10 µg L^{-1} Indium (In) and iridium (Ir) was employed as internal standards for all samples. The anaylzed masses of As (m/z75), Cd (m/z 112), Cr (m/z 52), Cu (m/z 65), pb (m/z 208), In (m/z 115) and Ir (m/z 193) were obtained by employing the mass spectrometer to sample ion intensities (peak jumping option).

Table 1 ICP-MS operating parameters applied for the measurement of total As, Cd, Cr, Cu and pb in digested vegetable samples.

ICP-MS	Agilent 7500 instrument	
	Peristaltic pump speed ml /min	1.0
	Nebulizer type	V-groove
	Spray chamber	Sturman-masters
	Radio frequency power (W)	1350
Gas flows (L min^{-1})	Coolant	12.4
	Auxiliary	0.9
	Nebulizer	0.8
H_2 addition	Gas flow (ml min^{-1}) 7 % H_2 in He	3.2
Dwell time (ms)	ICP-MS	10

2.3 Sampling and Sample preparation

A total of ten different vegetable samples were purchased from local markets in Erbil-Kurdistan Region-Iraq in April 2021. Table 2 shows the popular, scientific names and number of analysed samples. All samples were stored in sealed containers at the point of collection. These were then washed with Milli-Q water. All samples were dried using freeze drier for 48 hrs at -40 ºC. All dried samples were ground (using an agate pestle and mortar) and sieved to obtain 180 µm sample size using a nylon nylon180 µm sieve.

Table 2: Popular and scientific names, and the number of analysed vegetable samples

Common name	Scientific name	Total number of analysed samples
Chard	*Beta vulgaris subsp.*	3
Celery	*Apium graveolens*	3
Garden cress	*Lepidium sativum L.*	3
Spinach	*Spinacia oleracea*	3
Egyptian leek	*Allium Kurrat. Schweinf.*	3
Wild mint	*Mentha longifolia*	3
Spring onion	*Allium fistulosum*	3
Arum	*Arum spp*	3
Mallow	*Malva parviflora*	3
Sunflower	*Gundelia tournefortii*	3

2.4 Determination of total metals in vegetable samples

Acid digestion of vegetable samples was employed by a Mars Xpress microwave lab station (CEM, USA) using 100 mL capacity closed Teflon tubes with Teflon lids. The digestion of vegetable samples was based on Foulkes's el all (2020) publication. 0.25 g of freeze dried vegetable samples was weighed and transferred into separate

pre-cleaned Teflon reaction tubes followed by adding 5 ml HNO_3 (70%) and 2 mL H_2O_2 (30%) were put into each vessel. 1600 W was used for 43 min to conduct total digestion of all vegetable samples. The digestion process was performed as follows: the temperature ramped up to 160 ºC for about 15 min and continued at this temperature for another 5 min, then the temperature raised from

160 to 200 ºC in 8 min and continued at this temperature for an additional 15 min.

Once the digestion completed, the Teflon reaction tubes were permitted to cool down at room temperature. After the acid digestion was achieved, the samples were placed quantitatively into volumetric flasks (25 mL capacity) and completed to final 25 mL volume with 2% (v/v) HNO_3. In and Ir were added as internal standards to both the vegetable samples and standards (final concentration of 10 µg L^{-1}) for correction instrument drift (owing to sample viscosity effects, mass transport, etc.) throughout the analysis time, using ICP-MS. Total concentration of heavy metals including As, Cd, Cr, Cu and pb were validated in analysed vegetable samples using CRM (GBW10015-spinach).

3. Results and discussion

3.1 Results of CRM analyses for total heavy metals

Total As, Cd, Cr, Cu and Pb were determined in GBW10015-spinach for validation of the applied procedures. The analytical validity for, As, Cd, Cr, Cu and Pb were based on the use of CRM, GBW10015-spinach. This reference material was chosen to depict plant and vegetable samples. Good recoveries were obtained for total As, Cd, Cr, Cu and pb in the spinach with values of 109 and 96 % of the certified value, respectively. The results for total As, Cd, Cr, Cu and pb concentration in all CRMs are shown in Table 3.

3.2 Total Metals concentration in vegetables

The results of the content of heavy metals in the selected vegetable samples are given in Table 4. The bioaccumulation of heavy metals concentration in all the vegetables of this study are different, however, similar trends have been noticed for heavy metal concentration in seven vegetables of this study. The heavy metal bioaccumulation in chard, garden cress, Egyptian leek, wild mint, arum, mallow and sunflower was Cu > Cr > Pb > As > Cd, for celery was Cu > Cr > Pb > Cd > As, for spinach was Cr > Cu > Pb > As > Cd, for spring onion was Cu > Cr > As > Pb > Cd.

To validate the utilized method, total As, Cd, Cr, Cu and Pb were measured in the certified reference material GBW10015-spinach which showed satisfied recovery.

Table 3 CRM examination for total metals; all experimental values are given in µg g^{-1}, mean ± standard deviation (n=3)

Metals	Certified value	Experimental value obtained	Extraction efficiency %
Arsenic	0.230 ± 0.03	0.236 ± 0.017	103
Chadmium	0.150 ± 0.025	0.157 ± 0.003	105
Chromium	1.4 ± 0.2	1.45 ± 0.04	104
Copper	8.9 ± 0.4	8.521± 0.629	96
Lead	11.1 ± 0.9	12.1 ± 0.678	109

3.2.1 Arsenic

The concentration of As in the investigated vegetable samples varied from 0.160-0.436 µg g^{-1} (Table 4). The maximum concentration of As was found in spring onion, with a mean content for the triplicate measurements of 0.436 ± 0.007 µg g^{-1} dry weight (mean ± SD), while the minimum oncentration of As (0.160 µg g^{-1}) was detected in the celery. The concentration of As in chard (0.308 µg g^{-1}) was encountered to be higher than the result documented 0.09 µg g^{-1} by Gezahegn et al. (2017). The concentration of As in celery found in this study was similar to the values (0.154-0.196) obtained by Lin's et al (2014). Garden cress was contained 0.239 µg g^{-1} As which is lower than the concentration (0.095 µg g^{-1}) reported by Souri et al. (2018). The concentration of As in Egyptian leek (0.294 µg g^{-1}) was higher than the concentration (0.007 to 0.107 µg g^{-1}) obtained by Cheyns et al. (2017). The concentration of total As (0.215 µg g^{-1}) in wild mint was lower than that obtained by Rahman et al. (2007) which was 0.6 µg g^{-1}. The As content found in spinach (0.381 µg g^{-1}) and arum (0.239 µg g^{-1}) were higher than the concentrations, 0.015 µg g^{-1} and 0.175 µg g^{-1}, obtained by Khan et al. (2010) and Haque et al.(2020), respectively. The level of total As in spring onion (0.436 µg g^{-1}) was lower than the value reported by Mustățea et al. (2019) which was 3.59 µg g^{-1}. The As contents in Mallow and sunflower were found to be 0.409 µg g^{-1} and 0.198, respectively.

The maximum limit of As in vegetables has not been recommended yet. The statutory limit set for As concentration in fruit, crops and vegetables is 1.0 μg g^{-1} (fresh weight) (Carbonell-Barrachina et al., 2019). The concentration of As found in the vegetable samples (0.160-0.436) was lower than the mean concentration of As in plants which is 3.6 μg g^{-1} (Kabata-Pendias, 2000).

Inorganic forms of As are generally categorized to be the most poisonous species to humans (Jain, and Ali, 2000). The inorganic species of As tend to be predominant in plants (Jedynak et al., 2009; Jedynak et al., 2010) including a number of different crops and vegetables (Signes-Pastor et al., 2008; Smith et al. ,2009). Therefore, it can be concluded that the majority of As found in the investigated vegetables are inorganic forms which possess toxicological effect on human health.

3.2.2 Cadmium

The cadmium concentration (Cd) ranged from <LOD to 0.396 μg g−1 (Table 4). Cd was below the limit of detection of method (0.02 μg g^{-1}) in wild mint and arum. The maximum concentration of Cd detected in Mallow was 0.396 μg g−1 (Table 4).

The concentrations of Cd in chard (0.054 μg g^{-1}), garden cress (0.224 μg g^{-1}), spinach (0.182 μg g−1), Egyptian leek (0.059 μg g^{-1}), were lower than the concentrations (0.56 to 1.62 μg g^{-1}) documented by Mohamed et al. (2003) but higher than the concentration (0.04 μg g-1) reported by Bigdeli and Seilsepour, 2008). The Cd content in celery (0.329 μg g^{-1}) obtained was greater than that documented (0.03 to 0.152 μg g^{-1}) by Rusin et al. (2021). The present concentration 0.224 μg g^{-1} of Cd evaluated in garden cress was lower than the value obtained by Bigdeli and Seilsepour (2008) which was 1.25 μg g^{-1}. The Cd content in spring onion (0.037 μg g^{-1}) was lower than that reported (0.20 μg g^{-1}) by Naghipour et al. (2018). The concentration of Cd measured in Mallow and sunflower were 0.396 and 0.051 μg g^{-1}, respectively. According to WHO/FAO the recommended allowable safe limit for Cd in vegetables is 0.3 μg g^{-1} (Elbagermi et al., 2012). Thus, based on the findings obtained from this study, it could be concluded that the concentration of cadmium in vegetable samples did not exceeded the standard limit except the celery and Mallow samples.

3.2.3 Chromium

The level of Cr varied from 1.653 to 11.915 μg g^{-1}. Cr maximum concentration 11.915 μg g^{-1} was recorded in arum and lowest concentration 1.653 μg g^{-1} was obtained in spring onion as presented in Table 4. The concentrations of Cr in chard (4.456 μg g^{-1}) and celery (3.811 μg g^{-1}) were higher than results documented (0.07 and 0.14 μg g^{-1}, respectively) by Guerra et al. (2012). The level of Cr in garden cress (3.332 μg g^{-1}) and wild mint (5.023 μg g^{-1}) were higher than those documented (0.326 and 0.304 μg g^{-1}, respectively) by Mahdavi (2009). The concentration of Cr in spinach (11.075 μg g^{-1}) was higher than reported (6.625 μg g^{-1}) by Abdul Latif et al. (2018). In Egyptian leek, the Cr content in present study (2.904 μg g^{-1}) was in line with Taghipour and Mosaferi (2013), who reported to be 2.81 μg g^{-1}. The concentration of estimated Cd in spring onion, Mallow and sunflower were 1.653, 1.715 and 3.754 μg g^{-1}, respectively.

The concentration of Cr in all the vegetables exceeds than the allowed limit 0.1 μg g^{-1} by FAO/ WHO (Latif et al., 2018). Thus, the consumers were at risk because of high content of Cr and exceeding the allowable limit.

3.2.4 Copper

The concentrations of Cu ranged between 3.956 and 17.782 μg g^{-1} (Table 4). The lowest level detected in a sample of garden cress (3.956 μg g^{-1}) and highest concentration was found in arum (17.782 μg g^{-1}). The concentration of Cu in chard (8.498 μg g^{-1}), spinach (7.826 μg g^{-1}), Egyptian leek (9.754 μg g^{-1}) were higher than that obtained by Mohamed et al. (2003) for the same vegetables which were 1.86, 2.71 and 1.56 μg g^{-1}, respectively. The level of Cu in spring onion was 6.365 μg g^{-1} and higher than the Cu level (5.44 μg g^{-1}) obtained by Naghipour et al. (2018). The concentration of Cu in celery, 9.304 μg g^{-1}, was higher than the result of Zokaei et al. (2018) which was 2.91μgg^{-1}. The result for Cu level for garden cress, 3.956 μg g^{-1}, was higher than that obtained by Souri et al. (2018) for the same vegetable which was 2.11 μg g^{-1} (Souri et al., 2018). The results for Cu concentration in wild mint, 7.845 μg g^{-1}, was close to the results of Dghaim et al. (2015) which was between 3.82-12.32 μg g^{-1}. The concentrations of Cu in arum, Mallow, sunflower and were 17.782, 6.500 and 7.181 μg g^{-1}, respectively. However, the Cu content of all the vegetables of this study did not exceed the standard limit of FAO/WHO (40 μgg^{-1}) (Elbagermi et al.,2012).

3.2.5 Lead

The concentration of Pb found in the samples were in the range of 0.244-1.323 µg g^{-1} and all concentrations are calculated on dry weight basis (Table 4). The highest level of Pb (1.323 µg g^{-1}) was found in celery, and the lowest value was in spring onion with concentration of 0.244 µg g^{-1}. The concentration of Pb in chard (0.563 µg g^{-1}) and spinach (0.575 µg g^{-1}) were lower than the concentration (46.24 and 10.29 µg g^{-1}) reported previously in the study conducted by Mohamed et al. (2003).

Table 4 Total metal concentration in vegetables (µg g^{-1} dry weight**)**

Vegetable	As µg g^{-1} ± SD	Cd µg g^{-1} ± SD	Cr µg g^{-1} ± SD	Cu µg g^{-1} ± SD	Pb µg g^{-1} ± SD
Chard	0.308 ± 0.008	0.054 ± 0.003	4.456 ± 0.067	8.498 ± 0.041	0.563 ± 0.008
Celery	0.160 ± 0.007	0.329 ± 0.003	3.811 ± 0.040	9.304 ± 0.069	1.323 ± 0.025
Garden cress	0.239 ± 0.011	0.224 ± 0.006	3.332 ± 0.022	3.956 ± 0.036	0.466 ± 0.002
Spinach	0.381 ± 0.009	0.182 ± 0.005	11.075 ± 0.089	7.826 ± 0.083	0.575 ± 0.009
Egyptian leek	0.294 ± 0.009	0.059 ± 0.005	2.904 ± 0.028	9.754 ± 0.046	0.342 ± 0.006
Wild mint	0.215 ± 0.008	<LOD [a]	5.023 ± 0.095	7.845 ± 0.096	0.425 ± 0.005
Spring onion	0.436 ± 0.007	0.037 ± 0.001	1.653 ± 0.013	6.365 ± 0.070	0.244 ± 0.003
Arum	0.239 ± 0.011	<LOD [a]	11.915 ± 0.038	17.782 ± 0.255	0.272 ± 0.002
Mallow	0.409 ± 0.011	0.396 ± 0.014	1.715 ± 0.015	6.500 ± 0.033	0.782 ± 0.009
Sunflower	0.198 ± 0.009	0.051 ± 0.003	3.754 ± 0.045	7.181 ± 0.049	0.382 ± 0.001

[a] Concentration of Cd (0.019 µg g^{-1}) is below limit of detection of method

The concentration of Pb in Egyptian leek (0.342 µg g^{-1}) and spring onion (0.244 µg g^{-1}) of this investigation were lower compared to the study performed by Naghipour et al. (2018) which were 1.27 and 0.58 µg g^{-1}, respectively, while the concentration of Pb acquired in celery (1.323µgg^{-1}) was higher than the result of Guerra et al. (2012) and Rusin et al. (2021) which were 0.47 µg g^{-1} and 0.259, respectively. Regarding garden cress, the concentration of Pb was 0.466 µg g^{-1} and lower than that gained by Souri et al. (2018) which was 3.5 µg g^{-1}. Wild mint vegetable had lower concentration of Pb (0.425 µg g^{-1}) than that obtained by Dghaim et al. (2015) and Naghipour et al. (2018) which were 1.44 and 1.8 µg g^{-1}, respectively.

The concentrations of Pb in arum, Mallow and sunflower were 0.272, 0.782 and 0.382 µg g^{-1}, respectively.

The provisional tolerable weekly intake (PTWI) of Pb is 0.025 µg g^{-1} body weight. The maximum level of Pb in leafy vegetables recommended by FAO/WHO is 0.1-0.3 µg g^{-1} (Codex Alimentarius, 2016). Therefore, based on the findings obtained from this study, it could be concluded that the concentration of lead in all samples exceeded the standard limit except the arum sample.

3.3 Estimated daily intake

The estimated daily intake (EDI) of metals can be used to assess the average daily metals ingestion through consumption of vegetables by a specified bodyweight consumer. The value of EDI was calculated by the following equation (Zakaria et al, 2021):

$$EDI = \frac{C_{\mu g\, g^{-1}} \quad x \quad AV\ (kg/day)}{BM\ (Kg)} \qquad (1)$$

Where C is the mean heavy metal content in the vegetable (µg g^{-1}), AV is the vegetable intake consumed per day (kg/day), and BM is the mean body weight of the person (Kg). The WHO recommended to consume 300 to 350 g of vegetables daily per person in their diet. The mean 0.325 kg/person/day was used to calculate EDI.

In this study, a mean weight of person was recorded to be 65 kg (Gebreyohannes and Gebrekidan, 2018). Results of EDI are presented in Table 5.

Table 5 Estimated daily intake (EDI) of metals in adult through the consumption of vegetables.

Vegetable	As	Cd	Cr	Cu	Pb
Chard	0.0015	0.0003	0.0223	0.0425	0.0028
Celery	0.0008	0.0017	0.0191	0.0465	0.0066
Garden cress	0.0012	0.0011	0.0167	0.0198	0.0023
Spinach	0.0019	0.0009	0.0554	0.0391	0.0029
Egyptian leek	0.0015	0.0003	0.0145	0.0488	0.0017
Wild mint	0.0011	0.00	0.0251	0.0392	0.0021
Spring onion	0.0022	0.0002	0.0083	0.0318	0.0012
Arum	0.0012	0.00	0.0596	0.0889	0.0014
Mallow	0.0021	0.0020	0.0086	0.0325	0.0039
Sunflower	0.0010	0.0003	0.0188	0.0359	0.0019
WHO/FAO[b]	0.195[b]	0.05[b]	0.2[c]	3.25-32.5[b]	0.3[b]

[b](Codex Alimentarius, 2016)

c (Sultana et al, 2021)

3.4 Carcinogenic risk of trace metals

The carcinogenic risk of heavy metals from the ingestion pathway of each metals can be calculated as the following formul (Shaheen et al, 2016):

TR=(Efr x ED x FIR x C x SF)/(BW x AT) (2)

Where TR is carcinogenic risk of heavy metal or the risk of lifetime cancer, Efr is exposure frequency (365 days), ED is exposure duration (70 years for adult), FIR represents ingestion rate (0.325 kg), C is metal concentration (µg g^{-1}), AT represents the averaging time for carcinogens (365 days/year x ED) and BW is body weight (65 Kg).

SF is the oral carcinogenic slope factor is defined as the risk produced by a lifetime mean quantity of single mg/kg/day of carcinogen chemical and is contaminant specific (Mohammadi et al, 2019). The values of SF are 1.5, 6.1, 0.5, 0.0085 $(mg/kg/day)^{-1}$ for As, Cd, Cr and Pb respectively.

The carcinogenic risk of Cu was not estimated because of the lack of oral carcinogenic slope factor, however, the carcinogenic risks for other four metals (As, Cd, Cr and Pb) were evaluated and presented in Table 6.

The permissible levels of TR are considered to be 1.0E-6 and <1.0E-4 for an individual carcinogenic element and multi-element carcinogens (Živković et al., 2019). In the present work, carcinogenic risk through ingestion for all vegetables of As (1.20E-03 - 3.30E-03), Cr (2.80E-03-3.00E-02), and Pb (1.00E-05- 5.60E-05) were found to be higher than the acceptable range. Despite TRs for most of the vegetables exceeded the acceptable level (1.0E-6), the TR value for wild mint and arum is insignificant and lower than the acceptable value. The results of this work indicate that there is a cancer risk from heavy metals of As, Cd, Cr and Pb through consuming these vegetables.

Table 6 Target carcinogenic risk of heavy metals in analysed vegetables

Vegetable	As	Cd	Cr	Pb
Chard	2.30E-03	1.70E-03	1.10E-02	2.40E-05
Celery	1.20E-03	1.00E-02	9.50E-03	5.60E-05

Garden cress	1.80E-03	6.80E-03	8.30E-03	2.00E-05
Spinach	2.90E-03	5.60E-03	2.80E-03	2.40E-05
Egyptian leek	2.20E-03	1.80E-03	7.30E-03	1.50E-05
Wild mint	1.61E-03	0.00E+00	1.30E-02	1.80E-05
Spring onion	3.30E-03	1.10E-03	4.10E-03	1.00E-05
Arum	1.80E-03	0.00E+00	3.00E-02	1.20E-05
Mallow	3.10E-03	1.20E-02	4.30E-03	3.30E-05
Sunflower	1.50E-03	1.60E-03	9.40E-03	1.60E-05

4. Conclusion

The highest level of total As was found in spring onion with 0.436 µg g^{-1}, while lowest level total As was found in celery which was 0.160 µg g^{-1}. Cd concentration was found to be below the limits of detection in wild mint and arum samples, however, high concentration of Cd (0.396 µg g^{-1}) was detected in Mallow The results of this study showed that Cr and Cu were found in high concentrations in the investigated vegetables comparing with other examined heavy metals. In addition, the highest concentrations of both Cr and Cu were found in arum with 11.915 and 17.782 µg g^{-1}, respectively. However, the lowest concentration of Cr and Cu were found in the spring onion and garden cress with 1.653 and 3.956 µg g^{-1}, respectively. The highest level of Pb was found in a sample of celery with 1.323 µg g^{-1}, whilst lowest Pb concentration was found in spring onion which was 0.244 µg g^{-1}.
The high levels of certain heavy metals in some vegetable was consequence of the growing conditions of these vegetable samples in agricultural soils and irrigated water supply. The estimated daily intake for As, Cd, Cr, Cu and Pb in vegetables were in the range of 0.008-0.022, 0.002-0.020, 0.0083-0.0554, 0.0198-0.0889 and 0.0012-0.0066, respectively.
The estimated daily intake of As, Cd, Cr, Cu and Pb in vegetables were lower than the maximum tolerable daily intake values recommended by WHO/FAO. From human health prospective, the carcinogenic risk of single metals of 1.20E-03 - 3.30E-03), Cr (2.80E-03-3.00E-02), and Pb (1.00E-05- 5.60E-05) were found to be lower than the acceptable level (1.0E-06). This results indicated that there was adverse health and cancer risk from these heavy metals to residents who consumed these vegetables.

Conflict of Interest

The author has declared no conflicts of interest.

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