DOI: https://dx.doi.org/10.21123/bsj.2022.7253

Determination of essential and trace elements in various vegetables using ICP-MS

Rasul Jameel Ali [1] ***Bashdar Abuzed Sadee**** [2, 3]

[1]Department of Clinical Biochemistry, College of Health Sciences, Hawler Medical University, Erbil, Iraq.
[2]Department of Food Technology, College of Agricultural Engineering Sciences, Salahaddin University, Erbil, Iraq.
[3]Department of Nutrition and Dietetics, Cihan University-Erbil, Erbil, Iraq.
*Corresponding author: bashdar.sadee@su.edu.krd
E-mail address: rasul.ali@hmu.edu.krd

Received 4/4/2022, Revised 12/6/2022, Accepted 14/6/2022, Published Online First 20/11/2022
Published 1/6/2023

Abstract

Metal contents in vegetables are interesting because of issues related to food safety and potential health risks. The availability of these metals in the human body may perform many biochemical functions and some of them linked with various diseases at high levels. The current study aimed to evaluate the concentration of various metals in common local consumed vegetables using ICP-MS. The concentrations of metals in vegetables of tarragon, Bay laurel, dill, Syrian mesquite, vine leaves, thymes, arugula, basil, common purslane and parsley of this study were found to be in the range of, 76-778 for Al, 10-333 for B, 4-119 for Ba, 2812-24645 for Ca, 0.1-0.32 for Co, 201-464 for Fe, 3661-46400 for K, 0.31–1.53 for Li, 860-14330 for Mg, 16.20-71.5 for Mn, 612-4725 for Na and 15.8-46 µg g^{-1} for Zn. The results revealed that the concentration of Al, B except in Syrian mesquite, Ba, Ca, Fe, K, Mg and Mn in all analysed vegetables is higher than the recommended value, Li is well-within the safe limit, and Co, Na except in dill, arugula and common purslane, Zn are lower than the recommended intake of these elements. From health point of view, the HQ values for Al, Fe (for all vegetables) and Ba (in dill, vine leaves, thymes, arugula, basil, common purslane and parsley) were higher than one, indicating potential non-cancer health risk due to exposure to these metals. Furthermore, the HI value for all vegetables was higher than one, indicating potential non-cancer health risk due to long-term exposure to these metals.

Keywords: Hazard Index, Hazard Quotient, Heavy metals, ICP-MS, Validation.

Introduction

Human diets mainly contain plant materials because of their nutritional values. Minerals are classified as inorganic substances that exist in body tissues and fluids. Maintaining specific physicochemical processes which are crucial for human beings depends mainly on the presence of minerals. Despite their lack of ability to produce energy, they involve in a variety of body functions [1,2].

There are three classes of minerals: major minerals such as calcium (Ca), phosphorus (P), sodium (Na) and chloride (Cl); trace elements like iron (Fe), copper (Cu), cobalt (Co), potassium (K), magnesium (Mg), iodine (I), zinc (Zn), manganese (Mn), molybdenum (Mo), fluoride (F), chromium (Cr), selenium (Se) and sulphur (S); ultra-trace elements such as boron (B), silicon (Si), arsenic (As) and nickel (Ni) [2-7].

Heavy metals or metals can exist naturally in the environment, ecosystem and soils [8]. Metals such as Fe, Zn, Cu, Cd, Pb etc. have many applications in an industrial area in human life for example making pigments, paper, cement, metal alloys, rubber and other materials [9]. Human exposure to these elements occurs via air, water, soil and agricultural crops [10]. Minerals are transported into plant, animal, human tissues through respiration, food chain and industrial activities including anthropogenic processes, and affect the functioning of important cellular components [11-14]. When these heavy metals introduce into the human body, they provoke the immune system [14]. The insufficient amount of some minerals in the necessary quantity may have an adverse consequences on the immunity and growth of plants and humans through the food cycle [6].

Aluminum is the most abundant widespread metal in the environment and has enormous applications worldwide. The environment, diet and medications are the major routes of Al to enter the human body. However, a significant physiological role for Al within a human body has not been registered yet and can cause negative physiological consequences. Bioavailability and hence toxicity of Al depend mainly on acid environments. Biological systems are less likely to be affected by Al because a high quantity of Al is present in aluminosilicate soil minerals and low contents of Al are available in soluble type [15].

Boron is a fundamental mineral for plants. Despite of existence in animal tissue in small quantities and the possibility of being a crucial micronutrient for human beings, no major positive biochemical function is documented for animals and human beings. Shortened growth, losing of production, and even dying based on the extremity of deficiency are likely to be symptoms of B deficiency in plants. A high quantity of B can be toxic to plants and animals. Accumulation of B in animal and vegetable tissue results in a serious hazard to the health of those using food and water contaminated with high levels of B [16].

No biological function has been fully identified for Barium (Ba) but at high contents it is toxic to both animals and plants. In human beings, if the Ba content in the soil is 165-2000 µg g^{-1}, leads to several health diseases such as cardiac disorder and nervous system disorder, which subjects to death. However, an only a small quantity of Ba is present in the plant available form. It is reported that the chemical species of the element plays a major role in its availability, this characteristic measures its dissolution in the soil medium [17].

Calcium is considered an essential nutrient for plants. Divalent calcium cation (Ca^{+2}) involves in the structural components in the cell wall and membranes, it becomes counter-cation for inorganic and organic anions in the vacuole, and functions as an intracellular courier in cytosol [18]. The crystalline matrix of bone apparently contains calcium and phosphorous. Calcium uniquely contributes in stabilizing membranes, activating muscle contraction, promoting blood clotting and inducing cell signaling [19].

Cobalt is an essential element for higher plants. However, there is a lack of evidence for major function in their metabolism. Co is a crucial element in the general growth of plants. The process of stalk growth, maturity and healthy bloom development are mainly contributed by cobalt. Nevertheless, Co is an essential element, different negative consequences occur if over dosage of Co is induced. It is considered ~~as~~ an essential mineral for various enzymes and coenzymes. Co is an important element for the production of vitamin B12 which is necessary for human beings and animal diets [20].

If an excessive quantity of ingested iron accumulates in the body’s tissues, it may affect adversely on the body’s immune role, cell development and heart conditions. Anemia has resulted from iron shortened as oxygen is derived of body tissues, which is distinguished by its several indications for example a reasonable quantity of blood iron, low red blood cells and a small quantity of blood hemoglobin, faded, dizziness, susceptible to cold, antagonism, lack of concentration and heart pulsation [21,22].

In biological systems, potassium prevents fluidity of sodium into cells and leads to relaxation of contracted muscles, hence muscle cramps can be defeated by potassium salts or potassium-rich diets. This competition between the two involves serious especially once it intimidates the work of energy-dense sodium incline through membranes [19]. Different biochemical and physiological activities that help plants grow and develop depending on K content. Potassium leads to the synthesis of protein, metabolism of carbohydrates and active enzymes. The cation-anion equilibrium, osmoregulation, water flux, transferring of energy and some other operations are regulated by K [21].

Although the biochemical function of Lithium (Li) in the living organism systems is not certain, it is thought that it performs as a micronutrient. Sodium channels in the intestines adsorbs Li and it is measured in the serum, saliva and urine. Ingestion of extremely low doses of Li via drinking water may lead to various consequences such as anti-suicidal, stabilizing of mood, anti-depression and anti-insane effects. In addition, addressing dementia and Alzheimer’s sickness can be accomplished by consuming diets containing Li. Li can be ingested by humans through drinking water, grains, or vegetables [23].

It has been shown that there is a link between Mg deficiency and diseases such as osteoporosis in humans [24]. Mg is necessary for various of the essential member to act and it has an important function in human beings and animal physiology. Mg is crucial for the composition of bones and teeth, functions as a cofactor for greater than 300 enzymes in the body, containing carboxylases, phosphatases, protein kinases, RNA polymerases, and joining to ATP for kinase reactions, and influences porous of agitable membrane and neuromuscular transportation [24, 25]. In plant system, Mg helps to grow and reproduce plants because it is considered as an essential macronutrient for them. In addition, Mg plays a major role in photophosphorylation, CO_2 fixation by photosynthetic and metabolism, and partitioning of photo assimilates and usage [26, 27]

The health of the brain, tolerance of glucose, ordinary regeneration, and production of skeletal and cartilage can be resulted from manganese deficiency. Ingestion of excessive quantity of Mn may disturb both mental and emotional as well as make the movements of the body slow and clumsy [28].

Sodium alongside chloride ions controls water diffusion between cells, the interval fluid and plasma. The two ions Na and K are in everlasting dispute because the movement of Na ion is affected by K ion. Na ion does not have independently advantageous in the biological system. Blood pressure can be significantly controlled by sodium ions, hence one of the major factors in hypertension etiology is the presence of sodium ions in high quantity in the diet. Heart failure and other issues have resulted from hypertension which is recorded as a considerable health issue worldwide. Since one of the main functions of the kidney is controlling the sodium ion concentration of the blood and the amount of extracellular liquid, hypertension aggression targets primarily the kidney [19].

A significant quantity of Zn is accumulated in all living systems without causing any adverse consequences to them. Metabolism of carbohydrates, production of protein and elongation of inter nodal rely on the existence of Zn. It contributes to all biochemical processes and performs different functions in the continuation materials of genes and division of cells. If the quantity of Zn in dietary is not enough to assist these roles, Zn mal-absorption occurs because of abnormal biochemical processes and clinical symptoms. Deficiency of Zn causes deterioration of iron resulting in comparable signs [29].

The aim of this study was to quantify the levels of essential and trace elements present in different consumed common vegetables using ICP-MS and evaluate human health risk assessment through Estimated Daily Intake, Hazard Quotient and Hazard Index.

Materials and Methods:

Chemicals and Reagents

All chemicals used in this study were of analytical grade. All solutions were prepared using Milli-Q water (18MΩcm). Total Al, B, Ba, Ca, Co, Fe, K, Li, Mg, Mn, Na and Zn standards were prepared from the high purity stock solution 100 µg mL^{-1} in 5 %HNO_3 (CPI international, Peak performance, USA). Pure grade reagent of nitric acid 70 % (Merck, Germany) is utilized for the digestion of the sample. H_2O_2 37% was supplied by Fischer Scientific, United Kingdom. Spinach GBW10015 certified reference material (CRM) (Institute of Geophysical and Geochemical Exploration, Langfang, China) was purchased from LGC standards (Middlesex, UK).

Instrumentation

An Agilent 7500 ICP-MS (USA) instrument was used to perform total (27Al, 11B, 137Ba, 40Ca, 59Co, 56Fe, 39K, 7Li, 24Mg, 55Mn, 23Na and 65Zn) analysis. The instrument was equipped with a Modified Lichte spray chamber and a V-groove quartz nebulizer for sample introduction. The optimum operating conditions were as follow: radio frequency power of 1200 W with Argon (Ar) flow rates of 12.3, 0.8 and 0.95 L min^{-1} for cool, auxiliary and sample gas, respectively, dwell time of 10 millisecond.

Collision cell technology was equipped with ICP-MS to eliminate possible interferences and also 7 % H_2 in He with flow rates of 3.3 ml. min^{-1} was used. The measured isotopes of elements were Al (m/z 27), B (m/z 11), Ba (m/z 137), Ca (m/z 40), Co (m/z 59), Fe (m/z 56), K (m/z 39), Li (m/z 7), Mg (m/z 24), Mn (m/z 55), Na (m/z 23) and Zn (m/z 65). Theaccuracy of the applied procedure was validated using the certified reference material GBW10015-spinach. Indium (In) and iridium (Ir) were used as internal standards for all samples at a final concentration of 10 µgL^{-1} for correcting instrument drift. Edwards Super Modulyo freeze-drier (United Kingdom) was used to dry vegetable samples.

Sample preparation

Vegetable samples were collected from the local markets in Erbil city Kurdistan Region-Iraq in December 2021. Table 1 classifies the common and scientific names of analysed vegetable samples. Sealed containers were used to carry the vegetable samples from the point of collection. Milli-Q water was used to wash vegetable samples and placed them in a cooled plastic box. A freeze drier was utilized for 48 hours at -40 ºC for drying all vegetable samples. All dried vegetable samples were ground in an agate pestle and mortar to obtain a powder and a nylon 180 µm sieve was used to sieve to get a desired sample size. Brown glass bottles were used to store all samples for protecting them from light. Then finally all samples were placed in a desiccator to protect them from moisture until needed for analysis.

Table 1. Common vegetables and their scientific names of collected samples

Scientific names	Family	Common English name
Artemisia dracunculus L.	Asteraceae	Tarragon
Laurus nobilis L.	Lauraceae	Bay laurel
Anethum graveolens L.	Apiaceae	Dill
Prosopis farcta	Fabaceae	Syrian mesquite
Vitis vinifera L.	Vitaceae	Vine leaves
Thymus sp.	Lamiaceae	Thymes
Eruca sativa Mill.	Brassicaceae	Arugula
Ocimum basilicum L.	Lamiaceae	Basil
Portulaca oleracea L.	Portulacaceae	Common purslane
Petroselinum crispum (Mill.) Fuss	Apiaceae	Parsley

The general procedure for the determination of metals in vegetable samples

0.25 g of freeze dried samples was digested in separate 100 mL capacity closed Teflon vessels with 5 ml HNO_3 (70%) and 2 mL H_2O_2 (30%), the vessels were sealed and heated using a microwave lab station (Mars Xpress, CEM- USA) for 43 min total digestion time at 1600 W using a two steps and temperature program: in the first step of the digestion, the temperature ramp to 160 ºC over 15 min and hold at this temperature for a further 5 min, in the second step the temperature ramp from 160 to 200 ºC in 8 min and hold at this temperature for a further 15 min [30]. After digestion the Teflon reaction vessels were allowed to cool at room temperature and the samples were transferred quantitatively into precleaned volumetric flasks and diluted to volume 25 mL with 2% (v/v) HNO_3. The samples and standards were spiked with internal standards of In and Ir to give a final concentration of 10 µg L^{-1} during the measurement period, using ICP-MS. Three replicates per vegetable sample were measured. For After digestion the Teflon reaction vessels were allowed to cool at room temperature and the samples were transferred quantitatively into precleaned volumetric flasks and diluted to volume 25 mL with 2% (v/v) HNO_3. The samples and standards were spiked with internal standards of In and Ir to give a final concentration of 10 µg L^{-1} during the measurement period, using ICP-MS. Three replicates per vegetable samples were measured. For the quality control purpose, certified reference material (CRM) GBW10015- spinach was used for determination of Al, B, Ba, Ca, Co, Fe, K, Li, Mg, Mn, Na and Zn in different vegetable samples.

the quality control purpose, certified reference material (CRM) GBW10015- spinach was used for determination of Al, B, Ba, Ca, Co, Fe, K, Li, Mg, Mn, Na and Zn in different vegetable samples.

Health Risk Assessment of heavy metals

Risk assessment can be defined as the method of evaluating the possible existence of any identified possible quantity of the hurtful health consequence over an estimated time interval [31]. To evaluate the heavy metal contamination and non-carcinogenic health risk resulted from ingestion of heavy metal in the consumed vegetables of Erbil city, estimated daily intake of heavy metals (EDI), Hazard quotient (HQ) and Hazard Index (HI) were applied.

Estimated daily intake

EDI (mg/kg body weight/ day) of heavy metals from consumed vegetables was determined using the following equation [32]:

$$EDI = \frac{C \quad x \quad AV}{BM} \qquad 1$$

C is the average concentration of heavy metals in the vegetables of this study. AV is the vegetable consumption rate per day (Kg/day), and BM is the average body weight of person (Kg). The total daily intake of consumed vegetables in this study is 400 g $person^{-1}$ day^{-1} [33], and the average body weight of a person was registered to be 65 Kg [34].

Hazard Quotient (HQ)

The non-carcinogenic risk to humans from long term exposure to heavy metals from vegetables can be assessed by HQ. If HQ is less than one, this indicates that there is no potential health effect can be expected from exposure, whereas HQ more than one potential health risks are expected according to exposure. The HQ is assessed as a ratio of EDI to the reference dose as illustrated in the following equation [35]:

$$HQ=EDI/RfD \qquad 2$$

Where RfD is the oral reference dose of the metal (mg/kg/day). RfD for Al, Ba, Co, Fe and Zn is 1 mg/kg/day, 0.07 mg/kg/day, 0.03 mg/kg/day, 0.7 mg/kg/day, 0.3 respectively [36-40].

Hazard Index (HI)

The overall non-carcinogenic risks to human health for each kind of vegetable can be evaluated by HI. It is the summation of HQ of all heavy metals and can be denoted as following [35]:

$$HI = \sum HQAl + HQBa + HQCo + HQFe + HQZn \quad 3$$

If HI is more than 1 means that there is a high possibility of the adverse health effect related with exposure to this chemical [35].

Results and Discussion

Limits of detection

Instrumental limits of detection (LOD) for individual element were calculated from the slope obtained from calibration curves and three times standard deviations (SD) of 6 replicate blank measurements (3 X SD/slop of calibration curve) for each element. The LOD values for individual element using the ICP-MS (μg g^{-1}) were as follows: Al (0.02), B (0.2), Ba (0.001), Ca (0.001), Co (0.004), Fe (0.003), K (0.03), Li (0.04), Mg (0.01), Mn (0.02), Na (0.03) and Zn (0.003) which are convenience for the determination of selected metals in vegetables samples.

Validation of analytical method

The applied method was validated using GBW10015-spinach CRM for the quality control's purpose. Total concentration of Al, B, Ba, Ca, Co, Fe, K, Li, Mg, Mn, Na and Zn was determined in GBW10015-spinach followed by the digestion technique of developed method. The concentrations of selected metals in the CRM of GBW10015-spinach are presented in Table 2. The acquired concentrations of all metals except B and Mn from the experiment were well within the certified values for GBW10015-spinach as digestion efficiencies were in the range of 88 to 108%.

Table 2. CRM (GBW10015-spinach) concentrations of metals; all obtained data is given in μg g^{-1}, mean ± standard deviation (n=3)

Metals	Measured value	Certified value	Recovery %
Al	592 ± 50	610 ± 60	97
B	22 ± 1.03	25 ± 2	88
Ba	9.33 ± 0.34	9 ± 0.8	103
Ca	6617 ± 250	6600 ± 300	100
Co	0.239 ± 0.03	0.220 ± 0.03	108
Fe	522 ± 43	540 ± 20	96
K	24748 ± 800	24900 ± 1100	99
Li	1.325 ± 0.04	1.46 ± 0.23	91
Mg	5600 ± 300	5520 ± 150	101
Mn	36.615 ± 1.36	41 ± 3	89
Na	15082 ± 300	15000 ± 600	100
Zn	33.75 ± 2.93	35.3 ± 1.5	95

Vegetable heavy metals

The order of metal contents in vegetables is presented in Table 3. The contents of Al, B, Ba, Ca, Co, Fe, K, Li, Mg, Mn, Na and Zn in vegetables under study based on dry weight are presented in Table 4.

Table 3. The order of metal contents in analysed vegetables.

Metals	**Order of metals**
Tarragon	K > Ca > Mg > Na > Fe > Al > B > Mn > Zn > Ba > Li > Co
Bay laurel	Ca > K > Na > Mg > Al > Fe > B > Mn > Zn > Ba > Li > Co
Dill	K > Ca > Na > Mg > Fe > Al > B > Mn > Ba > Zn > Li > Co
Syrian mesquite	K > Ca > Mg > Na > Fe > Al > Mn > Zn > B > Ba > Li > Co
Vine leaves	Ca > K > Mg > Na > Al > Fe > B > Mn > Ba > Zn > Li > Co
Thymes	K > Mg > Ca > Na > Al > Fe > B > Mn > Ba > Zn > Li > Co
Arugula	K > Ca > Mg > Na > Al > Fe > B > Mn > Zn > Ba > Li > Co
Basil	Ca > K > Mg > Na > Al > Fe > B > Mn > Ba > Zn > Li > Co
Common purslane	K > Mg > Ca > Na > Al > B > Fe > Ba > Zn > Mn > Li > Co
Parsley	K > Ca > Mg > Na > Al > Fe > Ba > Mn > B > Zn > Li > Co

Aluminum

The mononuclear Al^{3+} species and Al_{13} are believed to be the most toxic species [15]. The lowest content of Al (76 µg g^{-1}) was detected in Syrian mesquite, whereas the highest level (778 µg g^{-1}) was found in vine leaves (Table 4). The recommended maximum permissible dose for Al is 60 mg/day [41,42]. The results of this study showed that all analysed vegetables of this study have Al contents more than this recommended dose.

Boron

In this study it is found that the distribution of B in all the samples varies in range 10 µg g^{-1} to 333 µg g^{-1}. The lowest content of B (10 µg g^{-1}) was found in Syrian mesquite, whereas the highest level (333 µg g^{-1}) was detected in common purslane (Table 4). The acceptable safe range of boron for adult is 1-13 mg/day [43]. The contents of boron in all vegetables except a Syrian mesquite were higher than the recommended acceptable safe range for B.

Barium

It has been reported that plants usually contain Ba in the range of 4 to 50 µg g^{-1} The highest level of Ba has been found in Brazil nuts which ranged from 3000 to 4000 µg g^{-1} [44]. The lowest content of Ba (4 µg g^{-1}) was found in Syrian mesquite, whereas the highest level (119 µg g^{-1}) was found in parsley (Table 4). The recommended long term dietary Ba intake for adults has been documented to be 0.6 mg/day from total diet and 1.24 mg/day for food only [45]. The concentration of Ba in all investigated vegetables except common purslane and parsley of this study is well-within the results of literature. However, these values are higher than the recommended dietary Ba intake.

Calcium

The lowest content of Ca (2812 µg g^{-1}) was detected in Syrian mesquite, whereas the highest level (24645 µg g^{-1}) was found in Arugula (Table 4). The Recommended Dietary Allowance for calcium for adult men and women is considered at a range between 1000 and 1300 mg/day [46]. The Ca level in analysed vegetables of this study is higher than the Recommended Dietary Allowance.

Cobalt

Opposite to other heavy metals consuming up to 8 mg of Co per day is safe and it doesn't impose health hazard [20]. The lowest content of Co (0.1 µg g^{-1}) was found in vine leaves, whereas the highest level (0.32 µg g^{-1}) was found in tarragon (Table 4). The maximum recommended permissible level of Co is 50 µg/day for adult [41,42]. The results of Co in vegetables of this research are less than the maximum recommended value so consuming these vegetables does not impose health hazards for Co.

Iron

The Recommended Daily Allowance for Fe is 10 to 30 mg depends on age and health circumstance [21]. The concentration of Fe in the analysed samples ranged between 201 and 464 µg g^{-1} were detected in common purslane and arugula, respectively (Table 4). The suggested Provisional Maximum Tolerable Daily Intake (PMTDI) of Fe has been set at 0.8 mg/kg body weight [41]. Therefore, for a 65 kg person the PMTDI is 52 mg. The concentrations of iron in vegetables of this study is higher than the recommended PMTDI.

Potassium

The lowest content of K (3661 µg g^{-1}) was found in Bay laurel, whereas the highest level (46400 µg g^{-1}) was found in arugula (Table 4). The adequate intake of potassium is considered to be 3500 mg/day for adult men and women [47]. The concentrations of K in all vegetables of this study are higher than the adequate intake of potassium.

Lithium

It has been reported that the content of Li in food sources are in the range of <0.001 and 4.238 mg/kg with vegetables [23]. The lowest content of Li (0.31 µg g^{-1}) was detected in Syrian mesquite, whereas the highest level (1.53 µg g^{-1}) was found in arugula (Table 4). The recommended daily allowance for Li for adult is set to be at 1mg /day [48]. The Li contents in vegetables of this study is comparable with the recommended daily allowance.

Magnesium

In this study it was found that the content of Mg in all the samples ranged from 860 µg g^{-1} to 14330 µg g^{-1}. The lowest content of Mg (860 µg g^{-1}) was found in Bay laurel, whereas the highest level (14330 µg g^{-1}) was detected in common purslane (Table 4). An adequate intake for Mg is set at 300 and 350 mg /day for adult women and men respectively [49]. The levels of Mg in investigated vegetables of this study are higher than an adequate intake.

Manganese

In the present study it was found that the content of Mn in all the samples varies in range of 16.20 µg g^{-1} to 71.5 µg g^{-1}. The lowest content of Mn (16.20 µg g^{-1}) was found in Syrian mesquite, whereas the highest level (71.5 µg g^{-1}) was detected in tarragon (Table 4). The recommended intake of Mn for an adult is 2-5 mg/day [41]. The concentrations of Mn in analysed vegetables are higher than the recommended value.

Sodium

The lowest content of Na (612 µg g^{-1}) was found in Syrian mesquite, while the highest level (4725 µg g^{-1}) was found in common purslane (Table 4). The recommended safe intake limit for Na for adult is 2 g per day [50]. The Na contents in all analysed vegetables except dill, arugula and common purslane are less than the recommended safe intake limit of sodium for adult.

Zinc

The concentration of Zn in the analysed samples ranged between 15.8 and 46 µg g^{-1} (Table 4). The lowest content of Zn (15.8 µg g^{-1}) was found in Syrian mesquite, whereas the highest level (46 µg g^{-1}) was detected in common purslane. The Provisional Maximum Tolerable Daily Intake (PMTDI) of Zn is 0.3-1.0 mg/kg body weight [41]. Therefore, for a 65 kg person the PMTDI value would be 19.5-65 mg. The Zn levels in vegetables of this study are lower than the PMTDI. The levels of Zn in analysed vegetables of this study are less than PMTDI.

Table 4. Concentration` of total metal (µg g^{-1}) in the vegetables based on dry weight (mean ± standard deviation)

Elements	Tarragon	Bay laurel	Dill	Syrian mesquite	Vine leaves	Thymes	Arugula	Basil	Common purslane	Parsley
Al	260 ±20	480 ±30	380 ±20	76 ±10	778 ±50	636 ±40	630 ±35	522 ±49	496 ±30	770 ±24
B	74 ±4	142 ±10	291 ±3	10 ±0.1	182 ±9	174 ±13	110 ±4	250 ±23	333 ±25	44 ±2
Ba	7.3 ±0.2	6.66 ±0.06	23.3 ±2.6	4 ±0.1	20.7 ±1	18 ±0.3	26.7 ±2.67	43.3 ±2	116 ±0.3	119 ±0.3
Ca	9954 ±550	6838 ±400	13326 ±600	2812 ±120	17167 ±500	6414 ±200	24645 ±500	22918 ±700	11205 ±500	13548 ±600
Co	0.32 ±0.02	0.192 ±0.02	0.19 ±0.01	0.22 ±0.01	0.1 ±0.01	0.174 ±0.01	0.224 ±0.02	0.3 ±0.02	0.11 ±0.08	0.11 ±0.01
Fe	402 ±12	302 ±14.8	432 ±35	268 ±3.7	235 ±32	443 ±17	464 ±9	306 ±24	201 ±14	270 ±15
K	28773 ±2300	3661 ±200	26902 ±1200	9123 ±650	7514 ±800	22347 ±500	46400 ±1500	18979 ±600	29395 ±650	27663 ±900
Li	1.25 ±0.06	0.59 ±0.03	0.94 ±0.02	0.31 ±0.04	1.2 ±0.01	1.04 ±0.01	1.53 ±0.03	1.1 ±0.03	1.3 ±0.01	1.04 ±0.01
Mg	4260 ±50	860 ±75	1950 ±170	1210 ±80	3330 ±210	6550 ±140	6760 ±400	6060 ±370	14330 ±201	2860 ±120
Mn	71.5 ±1.8	30.3 ±1.9	45.5 ±1.2	16.20 ± 2.3	39 ±1.86	32.8 ±1.7	38.3 ±3	45 ±4.9	31 ±3.1	66 ±2
Na	1565 ±45	1022 ±40	4062 ±200	612 ±25	902 ±30	1200 ±35	3724 ±100	1634 ±80	4725 ±100	1986 ±40
Zn	43 ±2	23.4 ±0.2	23 ±0.5	15.8 ±0.3	19.35 ±2.04	17.6 ±0.4	32 ±2	34 ±2	46 ±4	38 ±3

Health Risk Assessment of Heavy Metals

Daily intake plays a major role in the degree of toxicity of heavy metals to human. The consumption of these edible vegetables may cause human health risks to the consumers of these vegetables. The EDI values of heavy metals for population of this work are presented in Table 5. The maximum EDI value was registered as follows: Al in vine leaves; B, Mg, Na and Zn in common purslane; Ba in parsley; Ca, Fe, K and Li in arugula; Co and Mn in Tarragon, While the minimum values were as follows: Al, B, Ba, Ca, Li, Mn, Na and Zn Syrian mesquite; Co in vine leaves; Fe in common purslane; K and Mg in Bay laurel.

Table 5. EDI value of heavy metals in vegetables

Vegetable	Al	B	Ba	Ca	Co	Fe	K	Li	Mg	Mn	Na	Zn
Tarragon	1.60	0.455	0.045	61.26	0.0019	2.474	177.1	0.008	26.21	0.439	9.631	0.266
Bay laurel	2.95	0.874	0.041	42.08	0.0012	1.859	22.53	0.004	5.29	0.186	6.289	0.144
Dill	2.34	1.791	0.144	82.01	0.0012	2.659	165.6	0.006	12	0.279	24.997	0.141
Syrian mesquite	0.47	0.062	0.025	17.31	0.0013	1.649	56.14	0.002	7.45	0.099	3.766	0.097
Vine leaves	4.79	1.12	0.127	105.6	0.0006	1.446	46.24	0.007	20.49	0.237	5.551	0.119
Thymes	3.91	1.071	0.111	39.47	0.0011	2.726	137.5	0.006	40.31	0.202	7.385	0.108
Arugula	3.88	0.677	0.164	151.7	0.0014	2.855	285.5	0.009	41.6	0.235	22.917	0.194
Basil	3.21	1.539	0.267	141.0	0.0017	1.883	116.8	0.007	37.29	0.276	10.055	0.208
Common purslane	3.05	2.049	0.714	68.95	0.0007	1.237	180.9	0.008	88.19	0.192	29.077	0.285
Parsley	4.74	0.271	0.732	83.37	0.0007	1.662	170.2	0.006	17.6	0.405	12.222	0.233

The non-carcinogenic risk of the investigated heavy metals through the consumption of the selected vegetables of this study was determined by the HQ and the results are presented in Table 6. The results revealed that the HQ values for Co, Zn in all examined vegetables and Ba in tarragon, Bay laurel and Syrian mesquite were all smaller than one, indicating that the consumption of these vegetables is safe with no health risk due to these heavy metals. On the other hand, the HQ values for Al, Fe (for all vegetables) and Ba (in dill, vine leaves, thymes, arugula, basil, common purslane and parsley) are higher than one. It signifies that exposure through consumption of these vegetables poses a non-cancer risk due to overexposure to Al, Ba and Fe.

Furthermore, the risk value of HI was greater than one for all vegetables ranging from lowest (3.543) in Syrian mesquite and highest (18.374) in parsley (Table 6). This suggests that long-term exposure to these metals may poses potential non-carcinogenic health risk due to consuming these vegetables.

Table 6. HQ and HI via consumption of different vegetables

Vegetables	Al	Ba	Co	Fe	Zn	HI
Tarragon	1.600	0.644	0.045	3.534	0.886	6.709
Bay laurel	2.954	0.586	0.039	2.655	0.480	6.714
Dill	2.339	2.051	0.004	3.798	0.471	8.663
Syrian mesquite	0.468	0.352	0.044	2.356	0.323	3.543
Vine leaves	4.788	1.816	0.020	2.066	0.397	9.087
Thymes	3.914	1.582	0.036	3.895	0.360	9.787
Arugula	3.877	2.344	0.046	4.079	0.646	10.992
Basil	3.212	3.809	0.055	2.690	0.692	10.458
Common purslane	3.052	10.198	0.023	1.767	0.951	15.991
Parsley	4.739	10.462	0.023	2.374	0.776	18.374

Conclusion

The results of this study revealed a wide variability of essential and trace elements in analysed vegetables using ICP-MS followed by microwave assisted acid digestion of vegetables using nitric acid and hydrogen peroxide. The validity of the method was checked using certified reference material GBW10015 spinach and the results showed good extraction efficiency for the analysed minerals ranging from 91% to 108% except for B and Mn which were 88% and 89 respectively. This work showed that all chosen vegetables were a good source of different essential minerals such as sodium, potassium, magnesium, calcium, iron, zinc and manganese for plants and humans. However, a significant amount of trace metals such as Al, Ba, B, Co and Li were also identified in the selected vegetables, which may not be essential and their biological functions have not been recognized yet for humans.

From the health point of view, the HQ values for Al, Fe (for all vegetables) and Ba (in dill, vine leaves, thymes, arugula, basil, common purslane and parsley) were higher than one, signifying potential non-cancer health risk due to exposure to these metals. The HI value (HI>1) showed that the consumption of these vegetables can cause potential non-cancer risks due to consumption of these vegetables.

Author's declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Besides, the Figures and images, which are not ours, have been given the permission for re-publication attached with the manuscript
- Ethical Clearance: The project was approved by the local ethical committee in Hawler Medical University and Salahaddin University.

Authors' Contribution Statement

Rasul J. A. contributed in conception, acquisition of data, drafting the manuscript, interpretation, revision and proofreading. Bashdar A. S. participated in the conception, design, acquisition of data, drafting the manuscript, revision and proofreading.

Reference

1. Indrayan AK, Sharma S, Durgapal D, Kumar N, Kumar M. Determination of nutritive value and analysis of mineral elements for some medicinally valued plants from Uttaranchal. Curr Sci. 2005 Oct; 10: 1252-55.
2. Soetan KO, Olaiya CO, Oyewole OE. The importance of mineral elements for humans, domestic animals and plants-A review. Afri J food Sci. 2010 May 31; 4(5): 200-22.
3. Kabata-Pendias A, Mukherjee AB. Humans. Springer Berlin Heidelberg [Internet]. 2007 [Cited 2022 march 6]: 57-65. Available from: URL https://link.springer.com/book/10.1007/978-3-540-32714-1.
4. Nagajyoti PC, Lee KD, Sreekanth TV. Heavy metals, occurrence and toxicity for plants: a review. Environ Chem Lett. 2010 Sep; 8(3):199-216.
5. Dogan I, Ozyigit II, Demir G. Influence of aluminum on mineral nutrient uptake and accumulation in urtica Pilulifera L. J Plant Nutr. 2014 Feb 23; 37(3): 469-81.
6. Parvathy P, Murali VS, Devi VM, Murugan M, Jmaes JJ. ICP-MS assisted heavy metal analysis, phytochemical, proximate and antioxidant activities of Mimosa pudica L. Mater Today: Proc. 2021 Jan 1; 45: 2265-69.
7. Hamad AA, Alamer KH, Alrabie HS. The Accumulation Risk of Heavy Metals in Vegetables which Grown in Contaminated Soil. Baghdad Sci J. 2021; 18(3): 471-79.
8. Anjum S, Bazai ZA, Rizwan S, Benincasa C, Mehmood K, Siddique N, et al.. Elemental characterization of medicinal plants and soils from Hazarganji Chiltan National Park and nearby unprotected areas of Balochistan, Pakistan. J Oleo Sci. 2019; 68(5): 443-61.
9. Dzomba P, Chayamiti T, Togarepi E. Heavy metal content of selected raw medicinal plant materials: implication for patient health. Bull. Env. Pharmacol. Life Sci. 2012; 1: 28-33.
10. Järup L. Hazards of heavy metal contamination. Brit Med Bull. 2003 Dec 1; 68(1):167-82.
11. Gajalakshmi S, Iswarya V, Ashwini R, Divya G, Mythili S, Sathiavelu A. Evaluation of heavy metals in medicinal plants growing in Vellore District. Eur J Exp Biol. 2012; 2(5):1457-61.
12. Tahar K, Keltoum B. Effects of heavy metals pollution in soil and plant in the industrial area, West Algeria. J Korean Chem Soc. 2011; 55(6):1018-23.
13. Asati A, Pichhode M, Nikhil K. Effect of heavy metals on plants: an overview. Int J Appl Innov Eng Manag.2016; 5(3): 56-66.
14. Bradl, H. Heavy metals in the environment: origin, interaction and remediation, 1st edition, London: Acad Press, 2005. 86 p.
15. Nayak P. Aluminum: impacts and disease. Environ Res. 2002 Jun 1; 89(2):101-15.
16. Sah, RN. Brown, PH. Boron determination—a review of analytical methods. Microchemi J. 1997; 56: 285-304.
17. Kujawska J, Pawlowska M. Bioavailability of barium to Trifolium pratense L. in soils contaminated with drill cuttings. Int Agrophysics. 2019; 33(4): 417-26.
18. Pj W. Broadley MR. Calcium in plants. Ann Bot. 2003; 92(4): 487-511.
19. Harris ED. Minerals in food: Nutrition, metabolism, bioactivity. DEStech Publications, Inc; 2014 Jan 8. Available from https://www.destechpub.com/product/minerals-food-2/
20. Minz A, Sinha AK, Kumar R, Kumar B, Deep KP, Kumar SB. A review on importance of cobalt

in crop growth and production. Int J Curr Microbiol Appl Sci. 2018 Aug; 7: 2978-84.
21. Hasanuzzaman M, Bhuyan MH, Nahar K, Hossain MD, Mahmud JA, Hossen M, et al. Potassium: a vital regulator of plant responses and tolerance to abiotic stresses. Agronomy. 2018 Mar; 8 (3): 31 https://doi.org/10.3390/agronomy8030031.
22. Abdulkareem EA, Abdulsattar JO, Abdulsattar BO. Iron (II) Determination in Lipstick Samples using Spectrophotometric and Microfluidic Paper-based Analytical Device (µPADs) Platform via Complexation Reaction with Iron Chelator 1, 10-phenanthroline: A Comparative Study. Baghdad Sci J. 2022; 19(2): 355-67.
23. Török AI, Moldovan A, Levei EA, Cadar O, Tănăselia C, Moldovan OT. Assessment of Lithium, Macro-and Microelements in Water, Soil and Plant Samples from Karst Areas in Romania. Materials. 2021 Jan; 14(14): 4002. https://doi.org/10.3390/ma14144002 .
24. Rude RK, Gruber HE. Magnesium deficiency and osteoporosis: animal and human observations. J Nutr Biochem. 2004 Dec 1; 15(12): 710-16.
25. Long S, Romani AM. Role of cellular magnesium in human diseases. Austin J Nutr Food Sci. [Internet]. 2014; 2(10): 1051.:Available from https://austinpublishinggroup.com/nutrition-food-sciences/fulltext/ajnfs-v2-id1051.php.
26. Chaudhry AH, Nayab S, Hussain SB, Ali M, Pan Z. Current understandings on magnesium deficiency and future outlooks for sustainable agriculture. Int J Mol Sci. 2021; 22(4):1819. https://doi.org/10.3390/ijms22041819 .
27. Senbayram M, Gransee A, Wahle V, Thiel H. Role of magnesium fertilisers in agriculture: plant–soil continuum. Crop Pasture Sci. 2015 Dec 21; 66(12): 1219-29.
28. Gezahegn WW, Srinivasulu A, Aruna B, Banerjee S, Sudarshan M, Narayana PL, et al. Study of heavy metals accumulation in leafy vegetables of Ethiopia. IOSR J Environ Sci Toxicol Food Technol (IOSR-JESTFT). 2017; 11(5): 57-68.
29. Weldegebriel Y, Chandravanshi BS, Wondimu T. Concentration levels of metals in vegetables grown in soils irrigated with river water in Addis Ababa, Ethiopia. Ecotoxicol Environ Saf. 2012 Mar 1; 77: 57-63.
30. Foulkes ME, Sadee BA, Hill SJ. Arsenic speciation and its DNA fractionation in the rice plant Oryza sativa. J Anal Atom Spect. 2020; 35(9): 1989-2001.
31. Mohammadi AA, Zarei A, Majidi S, Ghaderpoury A, Hashempour Y, Saghi MH, et al. Carcinogenic and non-carcinogenic health risk assessment of heavy metals in drinking water of Khorramabad, Iran. Methodsx. 2019 Jan 1; 6: 1642-51.
32. Zakaria Z, Zulkafflee NS, Mohd Redzuan NA, Selamat J, Ismail MR, Praveena SM, et al. Understanding potential heavy metal contamination, absorption, translocation and accumulation in rice and human health risks. Plants. [2021 Jun; 10 (6): 1070. https://doi.org/10.3390/plants10061070 .
33. World Health Organization, Joint FAO/WHO Workshop on Fruit and Vegetables for Health, 2005. [Cited 2022 Feb 16]. Available from https://apps.who.int/iris/handle/10665/43143.
34. Gebreyohannes F, Gebrekidan A. Health risk assessment of heavy metals via consumption of spinach vegetable grown in Elalla river. Bull Chem Soc Ethiop. 2018 Apr 12; 32(1): 65-75.
35. Meseret M, Ketema G, Kassahun H. Health risk assessment and determination of some heavy metals in commonly consumed traditional herbal preparations in Northeast Ethiopia. J Chem.[Internet]. 2020 Dec 8. [cited 2022 Feb 20]; 2020: 1-7. https://doi.org/10.1155/2020/8883837 .
36. Antoine JM, Fung LA, Grant CN. Assessment of the potential health risks associated with the aluminium, arsenic, cadmium and lead content in selected fruits and vegetables grown in Jamaica. Toxicol Rep. 2017 Jan 1; 4:181-87.
37. Dallas E, Phillip L. Williams C. Barium: rationale for a new oral reference dose. J Toxicol Environ Health Part B: Crit Rev. 2001 Oct 1; 4(4): 395-429.
38. Sultana MS, Rana S, Yamazaki S, Aono T, Yoshida S. Health risk assessment for carcinogenic and non-carcinogenic heavy metal exposures from vegetables and fruits of Bangladesh. Cogent environ. Sci. 2017 Jan 1; 3 (1):1291107. https://doi.org/10.1080/23311843.2017.1291107.
39. Kamunda C, Mathuthu M, Madhuku M. Health risk assessment of heavy metals in soils from Witwatersrand Gold Mining Basin, South Africa. Int J Environ Res Public Health. 2016 Jul; 13(7): 663.
40. Javed M, Usmani N. Accumulation of heavy metals and human health risk assessment via the consumption of freshwater fish Mastacembelus armatus inhabiting, thermal power plant effluent loaded canal. Springer Plus. 2016 Dec; 5(1): 1-8.
41. Uluozlu OD, Tuzen M, Mendil D, Soylak M. Assessment of trace element contents of chicken products from Turkey. J. Hazard. Mater. 2009 Apr 30; 163(2-3): 982-87.

42. Nordberg, GF. Fowler, BA. Nordberg, M. Handbook on the Toxicology of Metals. 4th ed. Academic press, 2014. 339 p.
43. Nielsen FH. Boron in human and animal nutrition. Plant Soil. 1997 Jun; 193(1):199-208.
44. Monteiro FA, Nogueirol RC, Melo LC, Artur AG, da Rocha F. Effect of barium on growth and macronutrient nutrition in Tanzania guineagrass grown in nutrient solution. Comms Soil Sci Plant Analy. 2011 Jul 1; 42(13):1510-21.
45. World Health Organization, Barium in Drinking-water: Background Document for Development of WHO Guidelines for Drinking-Water Quality. (No. WHO/SDE/WSH/03.04/76), 2004. [Cited 2022 Jan 15]. Available from https://www.who.int/water_sanitation_health/water-quality/guidelines/chemicals/barium-background-jan17.pdf.
46. Ross AC, Taylor CL, Yaktine AL, Del Valle HB. Dietary reference intakes for adequacy: calcium and vitamin D. InDietary reference intakes for calcium and vitamin D. National Academies Press (US). 2011. 349 p.
47. Turck D, Bresson, J.-L, Burlingame B, Dean T, Fairweather-Tait S, Heinonen M. et al. EFSA Panel on Dietetic Products, Nutrition and Allergies (NDA), Dietary reference values for vitamin K. EFSA J. 2017 May; 15 (5) 4780. https://doi.org/10.2903/j.efsa.2017.4780.
48. Schrauzer GN. Lithium: occurrence, dietary intakes, nutritional essentiality. J Am Coll Nutr. 2002 Feb 1; 21(1):14-21.
49. European Food Safety Authority (EFSA), Panel (EFSA Panel on Dietetic Products, Nutrition and Allergies), Scientific Opinion on the evaluation of allergenic foods and food ingredients for labelling purposes. EFSA J. 2014; 12: 3894.
50. European Food Safety Authority (EFSA). Outcome of public consultations on the Scientific Opinions of the EFSA Panel on Nutrition, Novel Foods and Food Allergens (NDA) on Dietary Reference Values for sodium and chloride. 2019 Sep.; 16 (9): EN-1679. https:// doi:10.2903/sp.efsa.2019.EN-1679.

تحديد العناصر الأساسية و الشحيحة في الخضار باستخدام طيف الكتلة –بلازما الحث المقترن

رسول جميل على[1] **بشدار ابوزيد سعدى [2,3]**

[1]قسم الكيمياء الحيوية السريرية، جامعة هولير الطبية، أربيل، العراق.
[2] قسم الصناعات الغذائية، كلية الهندسة الزراعية، جامعة صلاح الدين - أربيل، العراق.
[3] قسم التغذية و الحميات، جامعة جيهان-اربيل، أربيل، العراق.

الخلاصة:

المحتويات المعدنية في الخضراوات مثيرة للاهتمام بسبب المشكلات المتعلقة بسلامة الأغذية والمخاطر الصحية المحتملة.. توفير هذه المعادن في جسم الإنسان قد يؤدي العديد من الوظائف البيوكيميائية وبعضها مرتبط بأمراض مختلفة عند مستويات عالية. الدراسة الحالية استهدفت إلى ايجاد تركيز المعادن المختلفة في الخضروات المحلية الشائعة المستهلكة باستخدام مطياف كتلة البلازما المقترنة بالحث ICP-MS. اظهرت الدراسة الحالية أن تراكيز المعادن في خضراوات الطرخون، ورق الغار، الباي، والشبت، والمسكيت السوري، وورق العنب، والزعتر، والجرجير، والريحان، والرجلة الشائعة، والبقدونس كان يتراوح في حدود ل 10-778 مع Al، لـ 10-333 مع B، لـ 4-1194 مع Ba، لـ 2812-24645 مع Ca ، لـ 0.1-0.32 مع Co، لـ 201-464 مع Fe، لـ 3661-46400 مع K، لـ 0.31-1.53 مع Li، لـ 860-14330 مع Mg، لـ 16.20-71.5 مع Mn، لـ 612-4725 مع Na، لـ 15.8-46 مع Zn ميكروغرام\ غرام. أظهرت النتائج أن تركيز Al، B باستثناء المسكيت السوري، Ba، Ca، Fe، K، Mg، Mn في جميع الخضروات التي تم تحليلها أعلى من القيمة الموصى بها، Li في حدود الحد الآمن و Co، Na باستثناء الشبت والجرجير والرجلة الشائعة، والزنك أقل من المدخول الموصى به من هذه العناصر. من وجهة النظر الصحية، تم استخدام المقدار اليومي المقدر(EDI)، وحاصل المخاطر(HQ) ومؤشر المخاطر(HI) من المعادن الثقيلة لتقدير تقييم المخاطر الصحية المرتبطة باستهلاك هذه الخضروات كانت قيم HQ لـ Al و Fe (لجميع الخضروات) و Ba (في الشبت وأوراق العنب والزعتر والجرجير والريحان والرجلة الشائعة والبقدونس) أعلى من واحد، مما يشير إلى احتمالية التعرض الخطرالصحى غير سرطانية بسبب التعرض لهذه المعادن. علاوة على ذلك ، كانت قيمة HI لجميع الخضروات أعلى من واحد، مما يشير إلى مخاطر صحية غير سرطانية محتملة بسبب التعرض الطويل الأمد لهذه المعادن.

الكلمات المفتاحية: مؤشر المخاطر، حاصل المخاطر، المعادن الثقيلة، ICP-MS ،تصديق