Health Risk Assessment of Heavy Metals in Some Selected Herbs and Spices from Local Egyptian Markets

Tarek A. Abd El-RAHMAN* and Ayman S.M. HASSAN

Pesticide Residue and Environmental Pollution Department, Central Agricultural Pesticide Laboratory, Agricultural Research Center, Dokki, Giza 12618, Egypt.

* ORCID: 0000-0002-1667-4857

Email: drtar5555@yahoo.com

Abstract: Determination of some essential (copper, iron and zinc) toxic metals (cadmium, chromium and lead) in anise, cumin, caraway, fennel, and fenugreek plants. Microwave digestion was used in the preparation of the samples.

Microwave plasma atomic emission spectroscopy was used in the measurements of the metals. Validation of the method was performed. The concentration of metals were within the allowed limits except for few samples. Concentration range for essential metals in herbs range from 0.45 to 3.9 mg/kg for copper, from 0.35 to 35.62 mg/kg for iron 0.002 and from 0.002 to 11.60 mg/kg for zinc. Toxic metal levels ranged between 0.45 to 1.980 mg/kg and 0.27-0.52 mg/kg for chromium and lead, respectively. Cadmium was detected only in fennel with a range between 0.18-0.4 mg/kg. Health risk assessment was calculated based on the analyzed sample results. The estimated risk assessment results for metals in anise, caraway and cumin plants had no adverse noncarcinogenic effects on human health, while the target metals in fennel and fenugreek represented a potential health issues due to their existence.

Keywords: Health Risk Assessment, Heavy metals, Herbs, Spices, MP-AES.

1. Introduction

The majority of ancient medications were made from plants. It is believed that 70-80% of the world's population uses nonconventional treatment, primarily herbal medicine (**Mihreteab *et al.*, 2020**). Herbs have long been used to cure and prevent ailments such as stomach discomfort, headaches, diabetes, hypertension, rheumatism, and many more. Spices have been used since prehistoric times. Archaeological excavations have shown that prehistoric man utilized the leaves of specific plants to taste the half-cooked meals he ate. The Phoenix (Greek and Roman ancient mythology) states: "From the hot hills and with rich spice frames, a pile shall burn, and Hatch him with his flames" **(Peter, 2013)**. A spice is a vegetal material of indigenous or alien origin that has or has a hot, spicy flavour and is used to enhance the flavour of dishes or to add stimulant substances to them (**Abban**, **2009**). Spices are becoming increasingly popular in Egyptian marketplaces **(Ayman and Abd El-Rahman, 2013)**. Heavy metals, herbicides, and/or poisons might contaminate these plants. It is critical to ensure that spices and medicinal plants are almost free of pollutants. Contamination of raw medicinal herbs and spices, as well as their products, is becoming more common **(Abdel Megeed *et al.*, 2014)**. This has raised questions and suspicions about practitioners' professionalism as well as the quality, efficacy, and safety of their treatment techniques and items derived from herbal and natural sources accessible on the market. Pollution in irrigation water, environment, soil, sterilization procedures, and storage conditions all play key roles in heavy metal contamination of medicinal plants in developing nations. Indeed, contamination of raw medicinal plants as well as their products is becoming more common **(Ayman and Abd El-Rahman, 2013).** This has raised worries and suspicions about practitioners' professionalism, as well as the quality, efficacy, and safety of their therapeutic techniques and items derived from herbal and natural sources that are accessible on the market. To safeguard customers from contamination, it is critical to maintain adequate quality control for therapeutic plants. Traditional medicine plays a significant influence in a population's overall health. Many therapeutic plants and their mixes can provide a health concern owing to the presence of toxic metals including Pb, Cd, Al, Hg, and Cr, which are poisonous to humans depending on their oxidation states and when present in high quantities **(Garcia *et al.*, 2000 and Lxozak *et al.*, 2002).**

Metals like, as Cu, Mn, and Zn are natural necessary components of enzymes and coenzymes that are required for growth, photosynthesis, and respiration. Despite the fact that other metals, such as Pb and Cd, have no biochemical or physiological significance, they are regarded very dangerous contaminants **(Sovljanski *et al*., 1990).** The most serious risks to human health from heavy metals are related with lead and cadmium exposure. Lead is a naturally occurring metal that is harmful in high concentrations **(Ona *et al*., 2006).** Cadmium is a heavy metal that is known to be hazardous to plants and is classed as a human carcinogen **(Deckert, 2005)**.

There are two primary reasons to monitor hazardous metal levels in medicinal plants **(Miclean and Cadar, 2021)**. To begin with, hazardous metal pollution of the general environment has grown. The origins of this pollution range from industrial and trace emissions to the use of agricultural expedients such as cadmium-containing dung, organic mercury fungicides, and the lead arsenate insecticide. Second, exotic herbal treatments, particularly those of Asian origin, have been linked to hazardous quantities of heavy metals on many occasions **(Schilcher *et al*., 1987).** Heavy metal toxicity is often caused by the ions' chemical interaction with cellular structural proteins, enzymes, and membrane systems **(Mahurpawar, 2015)**. Metals are non-biodegradable and accumulate in the environment, making them persistent contaminants **(Okatch, 2012).**

Food intake is the primary route of exposure to environmental pollutants **(González *et al*., 2019)**. Metal intake through ingestion is determined by dietary patterns. Thus, knowledge on metal consumption across the food chain is critical in determining the danger to human health **(Raghunath *et al*., 2006)**. The index of PTWI (provisional tolerable weekly intake) for each metal has been presented by the Joint Expert Committee on Food Additives from the World Organization of FAO and WHO **(Herrman, 1999)**. This index and the concentration derived from the plants were compared in this article, with the comparison being based on an estimate of the daily usage of medicinal herbs.

Different approaches (total diet study, journal study) can be used to assess the amount consumed from a meal, according to the FAO/WHO.

The health risk assessment is used to establish if any amount of a chemical may raise the likelihood of a harmful effect on human health (**Wcisło *et al*., 2002).** The goal of exposure evaluation is to identify possible receptors, evaluate exposure pathways, and quantify exposure.

Our aim of work was to establish the levels of chosen metals and examine the health risks associated with these metals.

2. Material and methods

The determination of metals in herb and spice samples were performed according to the method of the Association of Official Analytical Chemistry **(AOAC, 1995)**.

2.1. Sampling

Forty-five samples (nine of each of the five herbs and spices: anise, cumin, caraway, fennel, and fenugreek) were obtained from numerous local Egyptian marketplaces in 2022 (Table 1). The samples were packed in labelled plastic bags and promptly sent to the lab. All samples were kept at 2-5°C until they were analyzed. The samples were dried overnight at 70oC and allowed to cool before being analyzed. About 1.0 g of each dried sample was precisely weighed. The materials were then digested using a microwave digestion device with strong nitric acid. The samples were quantitatively transferred into 25 mL volumetric flasks and filled to the line with ultrapure water.

Table 1: Common and Scientific names, Families of Herbs, and Spices

Common name	Scientific name*	Family
Anise	*Pimpinilla anisum*	Umbellifeae or Apiaceae
Caraway	*Carum carvi*	Apiaceae
Cumin	*Cuminum cyminum*	Umbellifeae or Apiaceae
Fennel	*Foeniculum vulgare*	carrot family (Apiaceae)
Fenugreek	*Trigonella foenumgraecum*	Legomnoseae

***(Tamer *et al*., 2020)**

2.2. Chemicals and Standards

All chemicals, including nitric acid and standards, are of Analytical grade. Metals stock standards of Cd, Cr, Cu, Fe, Pb, and Zn were obtained from Merck, Darmstadt, Germany (1000 µg/mL).

2.3. Sample preparation

Microwave digestion was used to prepare the samples for measurements. Ten mL of HNO3 was added to accurately weighed (≈ 1.0 g) sample. A preloaded method for the MARS6 (CEM, Corporation, USA) microwave system was used to digest the samples. Once cooled, the solutions were diluted quantitatively to 25 mL using ultrapure water. The microwave digestion parameters were listed in Table 2.

Table 2: Microwave Digestion System Parameters

Options	Internal Fiber Optic Temperature Control Internal Pressure Control DuoTemp Control
Temperature	210°C
Pressure	800 psi
Time	**Ramp** : 21 min **Hold** : 15 min
Power	400- 1800
Vessels	EasyPrep Full Starter Set, P/T Control

2.4. Instrumentation

The Agilent microwave plasma atomic emission spectrometry (MP-AES) model 4200 was used for the measurements of metals concentration in the studied herbs and spices. Table 3 describes the instrumental parameters of the MP-AES. **(Cauduro, 2013)**. The MP-AES features continuous wavelength coverage, which allows the analyst to select wavelengths that are appropriate for the expected concentration range, and free from spectral interferences.

Table 3: Microwave Plasma Atomic Emission Parameters

Parameter	Value
Replicates	3
Pump rate	15 rpm
Sample uptake delay	15 seconds
Rinse time	30 seconds
Stabilization time	15 second
Fast Pump during Uptake and Rinse	On (80 rpm)
Nebulizer	OneNeb
Spray chamber	Double pass cyclonic
Autosampler	Agilent SPS 3
Sample pump tubing	Orange/green
Waste pump tubing	Blue/blue

Table 4: Metal Determined Wavelengths, Calibration Ranges and Correlation Coefficient

Metal	Wavelength (nm)	Calibration Range (µg/mL)	Correlation Coefficient (R^2)
Cadmium	228.8	0 – 2.500	0.9992
Chromium	425.4	0 – 2.000	0.9998
Copper	324.8	0 – 2.500	0.9992
Iron	372.0	0 – 2.500	0.9992
Lead	405.9	0 – 2.500	0.9999
Zinc	213.9	0 – 1.500	0.9904

2.5. Method Validation:

Method validation is an analytical technique for determining the dependability and reproducibility of analytical data. The analytical process was validated using parameters such as accuracy, precision, and limit of detection **(Kilic and Kilic, 2019)**. The following parameters were determined: linearity, repeatability, reproducibility, and LOQ. The samples were analyzed according to the recommended methods.

2.5.1. Linearity Factor:

Calibration curves for the six elements were built using at least three element concentrations and a blank (Table 4). Table 4 shows that the linearity of the calibration curves of the examined metals is R2= 0.9904 **-** 0.9999.

2.5.2. Limit of Detection and Limit of Quantification:

The method Limit Of Detection (LOD) =3 times the standard deviation of 10 measurements in blank matrix multiplied by the volume of the prepared solution and divided by the weight of sample in grams (LOD× Volume in mL/weight of the sample in g). The Limit of Quantification (LOQ) = 3times the LOD is defined as the lowest level of repeatabilities (at <10%) of the measurements. The Limit of Quantification of the studied six metals varied from 0.0083 µg/g for Cr to 0.3833 µg/g for Fe (Table 5).

2.5.3. Recovery and Uncertainty:

Percent recovery = concentration of spiked sample − concentration of unspiked sample × 100/ concentration of known spiked amount added. Accuracy was estimated from the recovery calculations.

Recovery percentage of five spiked samples with element concentrations at the level of LOD and five spiked samples with element concentrations at the level of 10 × LOD and the relative standard deviations of the replicated samples were calculated. The recovery percentage ranged from 94% to 103% at percentage standard deviation (%SD) of < 10%. This method has been validated at the laboratory scale with modifications. Absolute uncertainty was applied for the method validation. Precision values were based on the reproducibility parameters (relative standard deviations of the measurements)

Table 5: Method Limit of Detection (LOD) and Limit of Quantification (LOQ) and Percentage Recovery of the determined metals

Metal	*LOD (µg/g)	**LOQ (µg/g)	Recovery%
Cadmium	0.0525	0.1750	97%
Chromium	0.0025	0.0083	98%
Copper	0.0175	0.0583	98%
Iron	0.1150	0.3833	103%
Lead	0.0825	0.2475	94%
Zinc	0.1125	0.3375	96%

*LOD: The Limit of Detection (=3 times the standard deviation of 10 measurements in blank matrix)

**LOQ: The Limit of Quantification (= 3 times the LOD)

2.6. Health Risk Assessment calculations:

The estimated daily intake of metals, target hazard quotients, and total target hazard quotients for typical daily consumption in adults were used to assess human health risk **(Miclean and Cadar, 2021)**. The average daily intake, which is the measurement of the contaminant consumed, breathed, or absorbed through the skin, per kilogram body weight, per day, is used to estimate the dosage penetrated into the human body by contact with the contaminant (**Lim *et al*., 2008)**. Inhalation and cutaneous exposure can be ignored **(Miclean and Cadar, 2021)**. The values of the average daily intake of each metal in each food category (meat and organs, meat products, eggs, milk, cheese, animal fat, potato, vegetables, apple, bread, maize flour) and water were added together to get the average total daily food consumption of each metal. The water intake was included in the computation of daily metal intake, and the average amount consumed was taken into account. The average concentration of each metal analyzed in each food category was multiplied by the average amount of food consumed by a person/day in that location to get the daily intake of metals for each food category.

The estimated average daily intake (EDI) is determined by both the metal content in plants and the dosage of specific herbs consumed of Cadmium, Chromium, Copper, iron, lead and Zn EDIs were estimated using the average concentration of each element in each plant and the consumption rate. The ADI for heavy metal exposure in humans was determined using the following equation:

$ADI=C_m \times IR \times ABS \times EF \times ED/BW \times AT$ **(Zheng *et al*., 2020)**,

Where: ADI – the estimated average daily intake (mg/kg from BW/day);

C_m – the calculated metal concentration (mg/L or mg/kg);

IR – the daily ingestion rate per capita, is 0.5 g/day;

ABS – the absorption coefficient (=1);

EF – the exposure frequency was set 90 days per year;

ED – is the exposure days over a lifetime (20 year);

BW – the body weight, the average adult body weights were considered 65 kg;An adult's average daily intake of food is 20 g/person/day for an adult bodyweight of 65 kg **(Gebreyohannes and Gebrekidan, 2018)**.

AT – is the average lifetime (day) (AT = 60 years·365 days per year).

The daily intake of Cd, Cr, Cu, Fe, Pb and Zn for each studied herb or spice was estimated by multiplying the average concentration of each metal analyzed (C_m) in each food product by the average quantity of food consumed by a person/day in that region (FIR), according to equation:

$EDI = C_m \times FIR / BW$ (**Wang *et al*., 2019)**,

Where;

EDI is the estimated average daily intake of metal by food and water consumption (g/person/day).

FIR is the daily food ingestion rate (from each food product in mg/person/day).

C_m is the concentration of the metal in the in dry weight of food (mg/kg) = conc. of metal (mg /L) × Volume (L) / weight of the sample (g); BW is the average body weight (kg).

$THQ = EDI / R_fD$

$TTHQ = HI = \Sigma\ THQ_{Cd} + THQ_{Cr} + THQ_{Cu} + THQ_{Fe} + THQ_{Pb} + THQ_{Zn}$

FIR = daily food ingestion rate from each food category in mg/person/day;

The health risk from concurrent exposure to Cd, Cr, Cu, Fe, Pb, and Zn was calculated by finding the Total Target Hazard Quotients (TTHQ), which was derived by summing the individual THQ.

The Hazard Index (HI) or the Total Target Hazard Quotient (TTHQ) assesses the overall noncarcinogenic danger to human health posed by more than one heavy metal. Exposure to many pollutants has a compounding effect. It is then a method for determining the noncarcinogenic danger to people from long-term exposure to heavy metals found in food. The THQ is computed as a percentage of the determined dose divided by the reference dose, as stated in the equation: $THQ = EDI/R_fD$.

Where, EDI is the estimated daily intake of a food category (mg/kg/day) and R_fD is the metal's oral reference dosage (mg/kg/day) and refers to an approximation of the daily-tolerated exposure that a person is expected to endure without a substantial risk of adverse effects over the course of a lifetime.

If THQ < 1, there is no possibility of adverse noncarcinogenic effects on human health (**Akhtar *et al*., 2020)**. If the THQ = 1, no possible health impacts are predicted from exposure, while if THQ> 1 indicates that there are potential health concerns from exposure.

2.7. Statistical analysis:

Statistical calculations were carried out by means of **(SigmaStat computer software, 2012)**.

3. Results and discussion

3.1. Determination of Cadmium, Chromium, Copper, Iron, Lead and Zinc in Selected Herb and Spice Samples:

Chunhua Wu *et al*. (2012) used microwave plasma-atomic emission spectrometry to analyze Chinese herbal medicines. They stated that typical Chinese herbal medicines could be analyzed for trace and major concentration elements with good accuracy by preparing samples by microwave digestion and subsequent analysis by microwave plasma-atomic emission spectrometry. In addition, the MP-AES offers the lowest operating costs related to others techniques like flame AA, and by employing non-flammable gases, it eliminates the safety risks linked with acetylene and nitrous oxide. The installation of the Nitrogen Generator greatly reduces gas prices and allows for investigation in remote places where working gases are hardly attained.

Determination results of Chromium, Copper, Iron, Lead and Zinc (Cr, Cu, Fe, Pb and Zn) in herbal anise are summarized in Table 6. Chromium, copper, iron, lead and zinc concentration averages are 0.7267, 1.153, 10.23, 0.0600 and 6.216, repectively. Non-critical violation of the maximum permissible limits (2.3 and 0.3 mg/kg) for the toxic metals: Cr and Pb, can be observed **(OJEUC, 2006)**. Cadmium was not detected in any anise sample. Likewise, essential metals (Cu, Fe and Zn) have no elevation levels than the allowed limits (10, 300 and 50 mg/kg).

Table 6: Concentration of Cr, Cu, Fe, Pb, and Zn (mg/kg) in Anise

Herb	Cr	Cu	Fe	Pb	Zn
Anise	ND*	1.29	18.30	ND	5.300
	ND	0.5	16.20	ND	11.60
	ND	2.12	15.30	ND	10.30
	1.700	0.8	5.600	ND	3.770
	0.9800	0.6	5.400	ND	5.400
	0.9900	0.48	4.900	0.2700	5.960
	1.980	3.11	11.30	ND	4.620
	ND	0.65	6.800	0.2700	5.290
	0.8900	0.83	8.300	ND	3.700
Average	0.7267	1.153	10.23	0.0600	6.216
± SD**	0.7738	0.8980	5.199	0.1191	2.805
MPL***	2.3	10.00	300	0.3000	50.00

*ND = Not Detected (<LOQ) **SD = Standard Deviation ***MPL= Maximum Permissible Limit

Similarly, in Table 7 no hazardous levels of metals were found in caraway except one sample showed slightly higher concentration of lead than the permissible one. Cadmium, again, was not detected. Chromium average concentration is 0.3900 mg/kg. Lead average concentration is 0.0889 mg/kg. Only one of the caraway samples has higher level of Pb than the permissible one with a concentration of 0.52 mg/kg. The average concentrations of Cu, Fe and Zn are 1.88, 9.75 and 1.67 mg/kg, respectively.

No cadmium was detected in cumin. Chromuim average concentration is 0.4444 mg/kg (Table 8). Copper average concentration is 2.068 mg/kg. The average concentration of iron is 25.37 mg/kg. Only one cumin sample had Pb concentration of 0.41 mg/kg, which violated the allowed limits (0.3 mg/kg). The average concentration of Zn is 6.866 mg/kg.

Only two fennel samples were contaminated with cadmium with concentrations of 0.18 and 0.4 mg/kg with an average of 0.38 mg/kg (Table 9). One of these samples (with the concentration of 0.4 mg/kg) exceeded the maximum allowed limit (0.2 mg/kg). Four of nine samples of fennel had Cr concentrations with a range of 0.65-0.99 mg/kg and an average of 0.87 mg/kg. Copper in fennel samples was in the range of 0.63-1.6 mg/kg and average of 1.04 mg/kg. The average iron concentration is

Table 7: Concentration of Cr, Cu, Fe, Pb, and Zn (in µg/g) in Caraway

Herb	Cr	Cu	Fe	Pb	Zn
Caraway	1.6	1.290	16.3	ND	1.32
	ND	1.360	18.66	ND	1.52
	ND	2.330	12.03	ND	2.3
	ND	2.460	14.3	0.5200	1.4
	ND	3.900	7.56	0.2800	1.97
	ND	1.300	6.3	ND	1.66
	ND	1.600	4.3	ND	2.33
	0.92	1.300	5.2	ND	1.22
	0.99	1.400	3.1	ND	1.3
Average	0.3900	1.882	9.750	0.0889	1.669
± SD	0.6142	0.8817	5.696	0.1863	0.4301
MPL	2.300	10.00	300.0	0.3000	50.00

Table 8: Concentration of Cr, Cu, Fe, Pb, and Zn (in µg/g) in Cumin

Spice	Cr	Cu	Fe	Pb	Zn
Cumin	1.100	3.510	25.99	ND	10.20
	1.300	2.880	35.62	ND	3.560
	1.600	1.660	33.14	ND	2.690
	ND	1.630	28.66	ND	3.210
	ND	3.010	24.66	ND	8.400
	ND	2.110	29.33	ND	9.200
	ND	0.9800	16.45	ND	7.300
	ND	1.200	18.20	0.4100	8.110
	ND	1.630	16.30	ND	9.120
Average	0.4444	2.068	25.37	0.0456	6.866
± SD	0.6784	0.8743	7.125	0.1367	2.904
MPL	2.300	10.00	300.0	0.3000	50.00

0.6 mg/kg and range of concentrations is between 0.35 and 0.99 mg/kg. Lead had only one concentration in fennel of 0.32, which edges the maximum permissible limit (0.3 mg/kg). The concentration range for Zn is 0.002-0.09 mg/kg. The Zn average concentration is 0.01 mg/kg.

In Table 10, Cr concentration range is 0.48-1.22 mg/kg with a range of 0.91mg/kg. Copper concentration range is 0.45-1.65 mg/kg and their average is 0.98 mg/kg. The range for Fe is 19.99-35.21mg/kg and the average is 26.28 mg/kg. Two fenugreek samples had Pb concentration (0.33 and 0.35 mg/kg) that boundary the maximum allowed limits (0.3 mg/kg). Zinc average concentration is 2.06 mg/kg and the concentration range is 1.3-3.1 mg/kg.In general, Cd had an elevation level by 200% than the MPL in a single fennel sample. Chromium did not violate any concentration level than MPL in all the plant samples. Three samples (one of each of cumin, caraway, and fennel samples) exceeded the maximum allowed limits of Pb. Two fenugreek had higher concentrations than the maximum permissible limits. None of the essential metals (Cu, Fe or Zn) has contradicted any of the MPL.

In a previous work, monitoring of heavy metal levels in packed and unpacked herbs and medicinal plants was published **(Ayman and El-Rahman, 2013)**. Atomic absorption spectrophotometry was used for the identification and determination of the heavy metals, which were

Table 9: Concentration of Cd, Cr, Cu, Fe, Pb, and Zn (in µg/g) in Fennel

Herb	Cd	Cr	Cu	Fe	Pb	Zn
Fennel	ND	ND	0.9	0.96	ND	0.002
	ND	ND	0.98	0.66	ND	0.003
	ND	ND	0.63	0.59	ND	0.006
	ND	ND	0.77	0.99	ND	0.003
	0.4	ND	0.96	0.35	ND	0.006
	ND	0.99	1.5	0.36	ND	0.008
	0.18	0.96	1.02	0.39	ND	0.003
	ND	0.65	1.03	0.49	ND	0.003
	0.18	0.89	1.6	0.6	0.32	0.09
Average	0.0844	0.3878	1.043	0.5989	0.0356	0.0138
± SD	0.1417	0.4694	0.3155	0.2402	0.1067	0.0287
MPL	0.2000	2.3000	10.00	300.0	0.3000	50.00

Table 10: Concentration of Cr, Cu, Fe, Pb, and Zn (in µg/g) in Fenugreek

Herb	Cr	Cu	Fe	Pb	Zn
Fenugreek	1.3	1.06	35.21	ND	2.3
	1.22	1.03	26.59	ND	1.6
	0.99	0.99	27.33	0.35	1.9
	0.99	0.89	33.15	ND	1.32
	0.92	0.55	19.99	ND	2.99
	0.48	1.1	20.22	0.33	3.1
	0.75	1.09	21.36	ND	1.11
	0.99	1.65	28.33	ND	1.3
	0.55	0.45	24.31	ND	2.9
Average	0.9100	0.9789	26.28	0.0756	2.058
± SD	0.2756	0.3461	5.440	0.1501	0.7886
MPL	2.300	10.00	300.0	0.300	50.00

quantitatively determined as mg/kg in the collected samples. The highest mean levels of the metals were found in unpacked samples, while lower concentrations were found in the packed samples.A comparison can be performed with **Ayman Hassan (2015)** manuscript**.** Exploration of metal concentrations in some local spices by MP-AES after Microwave Digestion was there described. Cadmium was not detected then in 12 spice samples, while 10 other samples had higher levels than the maximum permissible limits (MPL). Chromium has been reported to have higher levels in almost all spice samples than the MPL. All the copper values were within the MPL. Half of the samples had higher contents of Fe than the MPL. Lead was not violating any of MPL. No zinc was found in spices to be higher than the MPL.

The quantities of heavy metals such as Pb, Cd, Co, and Se in common spices sold in Saudi Arabian marketplaces were evaluated using atomic absorption spectrometry **(Al-Eed *et al.*, 2002)**. The study found that metal concentrations were differed according to the edible portion (root, stem, leaf, and fruit, on a dry weight basis). Some of the concentrations were mentioned to exceed the WHO and FAO regulatory limit. The authors specified that there was no risk from daily consumption of the majority of spices under investigation containing the last harmful metals if humans consume only about 20 g of spices per day. However, they said that there was a risk from lead in basic, thyme, and ginger, cadmium was also dangerous in fenugreek.

Zinc, lead, nickel, mercury, copper, chromium, cobalt, cadmium and arsenic (µg/g) were detected in the commonly consumed herbal and culinary samples in Iraq according to the part used of the plant **(Hussien *et al.*,**

2023). They used ICP/MS for the determination of the former metals.

Mostafa *et al*. (2011) discovered that medicinal herbs tainted with Pb, Cd, As, and Al were within the safe limit. It was found that the plants were safe if employed for a short length of time or in tiny dosages. Washing was reported to significantly decrease surface contamination. As a result, they recommended that users should wash the medicinal herbs before using them.

3.2. Estimation of Health Risk Asses0sment of Cd, Cr, Cu, Fe, Pb and Zn in Anise, Caraway, Cumin, Fennel and Fenugreek

For estimating long-term exposure to metals through food intake, the average consumption over a given period of time and its reference-to-reference values on the amounts of metal (mg/kg body weight) that can be consumed daily and has adverse effects on health must be considered (**Wang *et al.*, 2019**).

The average daily intake of Anise in mg/kg/day (EDI = C_m × FIR)/BW).

Where,

C_m is the concentration of the metal in the in dry weight of food (mg/kg);

FIR is the daily food ingestion rate (from each food product in g/person/day),

BW is the average body weight (kg).

In Table 11, the THQ (Target Hazard Quotients) range for the five studied metals in anise between 0.0533 for Zn and 0.6229 for Cr and the Total THQ (TTHQ) is 0.9089. For caraway, the THQ range is 0.0143 for Zn – to 0.3343 for Cu and TTHQ is 0.6323. Cumin THQ range is 0.0589 for Pb - 0.3810 for Cu, while TTHQ is 0.8424. In fennel, THQ for the six metals is in the range of 0.0001 for Zn - 0.5771 for Cd, TTHQ is 1.008. Fenugreek THQ is in the range 0.0176 for Zn - 0.7800 for Cu and TTHQ is 1.192. The studied metals in anise, caraway and cumin had no possibility of adverse noncarcinogenic effects on human health (TTHQ<1). The contaminations of the target metals in fennel and fenugreek indicated that there are potential health concerns from exposure (TTHQ>1).

Miclean and Cadar (2021) investigated the dietary metals (Pb, Cu, Cd, Zn) exposure and their associated health risks in the Baia Mare area of northwestern Romania. According to the authors, that was due to the specific use of the soil in the investigated area, as well as the nature of the determined metals. They found that only one route of exposure was due to the ingestion of food by the resident population in the studied areas.

Shahedul *et al*. (2023) were meant to determine the concentrations of heavy metals Pb, Cd, Cr, Cu, and Fe in branded and unbranded spices collected from the Noakhali district of Bangladesh. Using the atomic absorption spectrophotometry method, as well as to assess the health hazard risk associated with heavy metal intake through spice consumption were applied. The highest quantities of Pb (15.47±1.93), Cd (1.65±0.011), Cr (31.99±3.97), Cu (18.84±1.97), and Fe (9.29±1.71) were discovered in Cardamom, Coriander leaf, Bay leaf, Dried chili, and Black pepper, respectively, by the authors. Estimated Daily Intake values (EDI) for Cr and Fe were 37% and 5% higher than reference doses (R_FD), respectively. Total Hazard Quotient (THQ) levels for Pb, Cd, Cu, and Fe were all found to be below the acceptable, while 37% of all spices had TTHQ values for Pb, Cd, Cu, and Fe that above the acceptable standard range. All the latter data were implying negative health consequences for consumers. Coriander, green chili, and ginger leaves, as well as some types of chili powder and turmeric powder, have been found to have extraordinarily high levels of Cr levels in TTHQ. Unbranded chili, green chili, and coriander leaf had an estimated carcinogenic risk effect that was higher than the safer levels

Conclusion

The results obtained showed no critical levels of the studied metals in the collected herbs and spices. The majority of samples had no violation of the maximum permissible limits of these metals except for lead which had five herb samples higher than the limits. The health risk assessments of the metals in anise, caraway and cumin plants had no adverse noncarcinogenic effects on human health. The target metals in fennel and fenugreek showed a potential health concerns due to their existence

Table 11: Health Risk Assessment Data of Metals in the Studied Herbs and Spices

Herb or Spice	RAP*	Cd	Cr	Cu	Fe	Pb	Zn	TTHQ*****
Anise	EDI**	-	0.0019	0.0030	0.0263	0.0003	0.0160	
	R_FD***	-	0.0030	0.0400	0.3000	0.0035	0.3000	0.9089
	THQ****	-	0.6229	0.07414	0.0877	0.0709	0.0533	
Caraway	EDI	-	0.0048	0.0010	0.0251	0.0003	0.0043	
	R_FD	-	0.0400	0.0030	0.3000	0.0035	0.3000	0.6323
	THQ	-	0.1210	0.3343	0.0836	0.0792	0.0143	
Cumin	EDI	-	0.0053	0.0011	0.0652	0.0002	0.0177	
	R_FD	-	0.0400	0.0030	0.3000	0.0035	0.3000	0.8424
	THQ	-	0.1329	0.3810	0.2175	0.0522	0.0589	
Fennel	EDI	0.0003	0.0027	0.0010	0.0015	0.00009	0.00004	
	R_FD	0.0005	0.0400	0.0030	0.3000	0.0035	0.3000	1.008
	THQ	0.5771	0.0671	0.332381	0.0051	0.0261	0.0001	
Fenugreek	EDI	-	0.0025	0.0023	0.0676	0.0004	0.0053	
	R_FD	-	0.0400	0.0030	0.3000	0.0035	0.3000	1.192
	THQ	-	0.0630	0.7800	0.2253	0.1061	0.0176	

*RAP = Risk Assessment Parameter **EDI= the estimated daily intake of Anise in mg/kg/day **(WHO, 2003)** *** R_FD = the metal's oral reference dosage (mg/kg/day) ****THQ = Target Hazard Quotients *****TTHQ = Total Target Hazard Quotients

References

Abban, Z. Y. (2009) Heavy Metal Contents of Some Local Spices on the Ghanaian Markets, M.Sc. Thesis, Kwame Nkrumah University of Science and Technology, College of Science, Chemistry Department.

Abdel Megeed, M. I.; T. A. AbdelRahman; M. M. Almaz and S. A. Dahroug, (2014) Pesticides residues in some medicinal plant samples collected from five Egyptian companies**,** J.Biol.Sci. .9 (1): 547-559.

Abou-Arab A. A. and Abou-Donia MA. (2000) Heavy metals in Egyptian spices, medicinal plants, and the effect of processing on their levels. J Agricultural Food Chem, 48 (6):2300-2304.

Akhtar S, Riaz M, and Naeem I, Gong YY, Ismail A, Hussain M, *et al*. (2020) Risk assessment of aflatoxins and selected heavy metals through intake of branded and non-branded spices collected from the markets of Multan city of Pakistan. Food Control, 112:107132.

Al-Eed, M. A., F. N Assubaie, M. M. El-Garawany*, H. EL-Hamshary and Z. M. ElTayeb (2002) Determination of Heavy Metal Levels in Common Spices, Egy J App Sci.

AOAC (1995). Assoc. Official Anal. Chem., 16th ed. AOAC Int., Arlington, Virginia, USA.

Ayman S.M. Hassan (2015) Exploration of Metal Concentrations in Some Local Spices by Microwave Plasma Atomic Emission Spectrometry after Microwave Digestion, Egy Sci J Pestic.

Ayman S.M. Hassan and Tarek. A.A. Abd El-Rahman, (2013) Monitoring OF the heavy metals levels in SOME HERBS AND MEDICINAL PLANTS (packed and unpacked), Proc. of The International Conference of Environmental Sciences (ICES), 23 – 32.

Cauduro, J.; (2013). Determination of major, minor and trace elements in rice flour using the 4200 Microwave Plasma- Atomic Emission Spectrometer (MP-AES) , Agilent Technologies, (available on (https://docs.google.com/viewer?url=http://www.chem.agilent.com/Library/applications/5991-3777EN.pdf) last accessed on January 7, 2015).

Choi, Dr Y.Y. (2011) International / National Standards for Heavy Metals in Food, Cap. 132V Food Adulteration (Metallic Contaminants) Regulations First Schedule: Maximum permitted concentration of certain metals naturally present in specified foods.

Chunhua, W.; Y. Chen; K. Ouyang; Z. Zhang; and C. Taylor, (2012). Analysis of Chinese herbal medicines by microwave plasma-atomic emission spectrometry (MP-AES), (available on (https://docs.google.com/viewer?url=http://www.chem.agilent.com/Library/applications/5990-9791EN_AppNote_4100MP-AES Chinese Medicines.pdf) last accessed on June 14, 2015)

Codex (1993) Codex Alimentarius Commission, Joint FAO/WHO Food Standards Program.

CODEX GENERAL STANDARD FOR FOOD ADDITIVES (1995) CODEX STAN 192, PREAMBLE

Deckert, J. (2005) Cadmium toxicity in plants: Is there any analogy to its carcinogenic effect in mammalian cells Bimetals, 18(5), 475–481.

Garcia E, Cabrera C, Lorenzo ML, Lo´pez MC. (2000) Chromium levels in spices and aromatic herbs. Sci Total Environ, 247:51– 6.

Gebreyohannes; F. and A. Gebrekidan (2018) Health risk assessment of heavy metals via consumption of spinach vegetable grown in Elalla river," *Bulletin of the Chemical Society of Ethiopia*, 32, 1, 65–75.

González N, Calderón J, Rúbies A, Timoner I, Castell V, Domingo JL, Nadal M. (2019) Dietary intake of arsenic, cadmium, mercury and lead by the population of Catalonia, Spain: Analysis of the temporal trend, Food Chem Toxicol., 132, 110721.

Herrman J. (1999) Risk analysis of mycotoxins by the Joint FAO/WHO Expert Committee on Food Additives (JECFA).

Hussien Aliwy Hassan Al-keriawy, Sundus Saleh Nehaba, Saad Wali Alwan (2023) Environmental Risk Assessment of Heavy Metals in Selected Medicinal Herbs and Spices, Journal of Ecological Engineering, 24, 6, 376–384.

Kilic; M, S. Kilic (2019) Method Validation for the determination of toxic elements in fizzy fruity mineral water drinks using ICP-MS, Eurasian J. Bio. Chem. Sci. 2, 38–41.

Krejpcio, Z.; E. Król; and S. Sionkowski; (2007) Polish J. of Environ. Stud., 16, 1, 9 7-100.

L Xozak A, Soytyk K, Ostapczuk P, Fijayek Z. (2002) Determination of selected trace elements in herbs and their infusions, Sci Total Environ, 289, 33– 40.

Lim HS, Lee JS, Chon HT, Sager M. (2008) Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon Au-Ag mine in Korea. J Geochem Explor, 96, 223-230. https://tinyurl.com/4brh7jt6

Mahurpawar, M. (2015) Effects of heavy metals on human health, International Journal of Research-Granthaalayah, 530, 1–7.

Miclean, Mirela and Oana Cadar (2021) Dietary Metals (Pb, Cu, Cd, Zn) Exposure and Associated Health Risks in Baia Mare Area, Northwestern Romania, Journal of Biomedical Research & Environmental Sciences, 2,7, 581.

Mihreteab Meseret, Gebremariam Ketema, and Haile Kassahun (2020) Health Risk Assessment and Determination of Some Heavy Metals in Commonly Consumed Traditional Herbal Preparations in Northeast Ethiopia, Hindawi Journal of Chemistry, Volume 2020, Article ID 8883837, 7 pages, https://doi.org/ 10.1155/2020/8883837.

Molla Tefera, Almaz Teklewold (2021) Health risk assessment of heavy metals in selected Ethiopian spices, Heliyon, 7.

Mostafa Delavar, Gholam Reza Asghari, Farya Amiri, Mahdi Abdollahi (2011) The Study of Toxic Metals Contamination (Pb, Cd, As, Al) on Medicinal Plants Cultivated Near Arak Industrial Manufactures, Iranian Journal of Toxicology, 5, 14.

Nkansah, M. A. and C. O. Amoako, (2010) American Journal of Scientific and Industrial Research, 1.2.158.163.

Official Journal of the European Union Commission (OJEUC, 2006) Regulation No 1881/2006

Setting Maximum levels for Certain Contaminants in Foodstuffs.

Okatch; H. B. Ngwenya, K. M. Raletamo, and K. Andrae-Marobela, (2012) Determination of potentially toxic heavy metals in traditionally used medicinal plants for HIV/AIDS opportunistic infections in Ngamiland District in Northern Botswana, Analytica Chimica Acta, 730, 42–48.

Ona, L. F., Alberto, A. M., Prudente, J. A., & Sigua, G. C. (2006) Levels of lead in urban soils from selected cities in a central region of the Philippines. Environmental Science and Pollution Research, 13, 3,177–183.

Peter, K. V. (2013) Handbook of Herbs and Spices, Vol.1, Woodhead Publishing Limited, Cambridge, England.

Raghunath R, Tripathi RM, Suseela B, Bhalke S, Shukla VK, Puranik VD.(2006) Dietary intake of metals by Mumbai adult population. Sci Total Environ., 1, 356, 1-3, 62-68.

Raouf A. L. M.; K. K. Hammud; and S. K. Zamil; (2014) International Journal of Pharma Sciences and Research, 5, 11.

Schilcher, H., Peters, H., and Wank, H. (1987) Pesticide und Schmermretalle in Arzneipmanzen and Arzneiplanzen Zubereitun-gen. Pharm. Ind., 49, 202-211.

Shahedul Islam, Akibul Islam Chowdhury, Lincon Chandra Shill, Sompa Reza and Mohammad Rahanur Alam (2023) Heavy Metals Induced Health Risk Assessment Through Consumption of Selected Commercially Available Spices in Noakhali District of Bangladesh, medRxiv.org - the preprint server for Health Sciences, https://creativecommons.org/licenses/by/4.0/

SigmaStat computer software (2012) https://systat software.com

Sovljanski, R., Lazic, S., Macko, V., and Obradovic, S. (1990) Heavy metals contents in medicinal and spice plants cultivated in Yugo-slavia. Herba-Hungarica, 29, 3, 59, 63.

Tamer M. A. M. Thabit , Dalia I. H. Elgeddawy, and Shokr Abdelsalam Shokr (2020) Determination of Some Common Heavy Metals and Radionuclides in Some Medicinal Herbs Using ICP-MS/MS, Journal of AOAC INTERNATIONAL, 103, 5, 1282–1287.

Wang M, Liang B, Zhang W, Chen K, Zhang Y, Zhou H, Cheng Y, Liu H, Zhong X, Li Y, Liu Y. (2019) Dietary lead exposure and associated health risks in guangzhou, china., Int J Environ Res Public Health, 19, 16, 8, 1417.

Wcisło E, Ioven D, Kucharski R, Szdzuj J. (2002) Human health risk assessment case study, An abandoned metal smelter site in Poland. Chemosphere, 47, 5, 507-515.

World Health Organization (WHO/ 2003) GEMS/Food Regional Diets: Regional per Capita Consumption of Raw and Semi-processed Agricultural Commodities. Food Safety Department/World Health Organization, Geneva, Switzerland, Septempter 2003.

World Health Organization (WHO/ 2019) Global Report on Traditional and Complementary Medicine.

Zheng, L., Zhang, Q., Li, Z., Sun, R., Zhong, G. (2020) Exposure risk assessment of nine metal elements in Chongqing hotpot seasoning, RSC advances, 10, 4, 1971–1980.

تقييم المخاطر الصحية للمعادن الثقيلة في بعض الأعشاب والتوابل المختارة من الأسواق المصرية المحلية

طارق عبد العليم عبد الرحمن - أيمن السيد محفوظ

المعمل المركزى للمبيدات - مركزالبحوث الزراعية ، شارع نادى الصيد بالدقى ، الجيزة ، مصر

الملخص العربى:

تحديد بعض المعادن الأساسية السامة (النحاس والحديد والزنك) (الكادميوم والكروم والرصاص) في نباتات اليانسون والكمون والكراوية والشمر والحلبة. تم استخدام الهضم بالموجات الدقيقة في تحضير العينات.

تم استخدام مطيافية الانبعاث الذري لبلازما الميكروويف في قياسات المعادن. تم إجراء التحقق من صحة الطريقة. كان تركيز المعادن ضمن الحدود المسموح بها باستثناء عينات قليلة. يتراوح تركيز المعادن الأساسية في الأعشاب من ٠,٤٥ إلى ٣,٩ مجم / كجم للنحاس، ومن ٠,٣٥ إلى ٣٥,٦٢ مجم / كجم للحديد ٠,٠٠٢ ومن ٠,٠٠٢ إلى ١١,٦٠ مجم / كجم للزنك. تراوحت مستويات المعادن السامة بين ٠,٤٥ إلى ١,٩٨٠ مجم / كجم و ٠,٢٧-٠,٥٢ مجم / كجم للكروم و للرصاص. على التوالي وتتراوح بين ٠,١٨-٠,٤ مجم / كجم للكادميوم في الشمر فقط، تم حساب تقييم المخاطر الصحية بناءً على نتائج العينة التي تم تحليلها. نتائج تقييم المخاطر التقديرية للمعادن في نباتات اليانسون والكراوية والكمون لم يكن لها آثار ضارة غير مسرطنة على صحة الإنسان، في حين أن المعادن المستهدفة في الشمر والحلبة تمثل مشاكل صحية محتملة بسبب وجودها.

الكلمات المفتاحية: تقييم المخاطر الصحية، المعادن الثقيلة، الأعشاب، البهارات، MP-AES.