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INVESTIGATION OF HEAVY METALS IN FRUITS AND VEGETABLES AND THEIR POTENTIAL RISK FOR EGYPTIAN CONSUMER HEALTH

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Abstract

Fruits and vegetables are edible plant products that are good for health. Precise qualitative and quantitative analyses of heavy metals present in them are important for accurate nutritional labelling, determination of compliance with the standard of identification and in ensuring that the products meet manufacturer's specification.

A total of seventy samples of different fruits and vegetables collected from the different Egyptian local markets located in Giza. All collected samples were subjected to heavy metals analysis by microwave digestion and determination by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES), to investigate the cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), tin (Sn) and zinc (Zn) elements. The results showed that the concentration ranges, in mg/kg, were as follows: for (Cd) < 0.02 – 0.12, < 1 – 1.5 (Cr), < 1 – 5.5 (Cu), 1.5 – 768 (Fe), < 0.05 – 0.35 (Pb), < 1 – 40.1 (Mn), < 1 – 5.6 (Ni) and < 1 – 492.9 (Zn) all analyzed samples. However, the concentration level On the other hand, all detectable amount of Co, and Sn in all tested samples were found to be less than the quantifications limits. The daily intakes of essential elements (Cr, Cu, Fe, Mn, Ni and Zn) are lower than the limits in vegetables stated by Egyptian standards. Similarly, the weekly intakes of Cd and Pb were also significantly below the recommended tolerable levels.

Key words: Fruits, Vegetables, Essential and toxic metals, ICP OES, Dietary intake, Egypt.

Introduction

Fruits and vegetables are very important protective food and useful for the maintenance of health and the prevention and treatment of various diseases (D'Mello, 2003). The great importance of fresh fruits and vegetables are because of they are rich sources of vitamins, minerals, and fibers and also have beneficial antioxidative effects. In addition, they contain water, calcium, iron, sulphur and potash (Sobukola *et al.,* 2010). However, these plants contain both essential and toxic metals over a wide range of concentrations (Radwan and Salama, 2006).

The effect of heavy metal contamination of fruit and vegetables cannot be underestimated as these foodstuffs are important components of human diet. However, the intake of heavy metal-contaminated fruit and vegetables may pose a risk to human health; hence the heavy metal contamination of food is one of the most important aspects of food quality assurance (Radwan and Salama, 2006; Wang *et al.,* 2005 and Khan *et al.,* 2008). Heavy metals, in general, are not biodegradable, have long biological half-lives, and have the potential for accumulation in different body organs, leading to unwanted side effects (J¨arup, 2003 and Sathawara *et al.,* 2004). Plants take up heavy metals by absorbing them from airborne deposits on the parts of the plants exposed to the air from the polluted environments as well as from contaminated soils through root systems. Also, the heavy metal contamination of fruit and vegetables may occur due to their irrigation with contaminated water Al Jassir *et al.,* 2005.

The levels of heavy metals (lead, cadmium, copper, and zinc) have been examined in selected fruits and vegetables sold in local Egyptian markets (Radwan and Salama, 2006). Fytianos *et al.,* 2001 studied the contents of heavy metals in vegetables grown in an industrial area of Northern Greece, and Sobukola *et al.,* 2010 investigated the concentrations of some heavy metals in fruits and leafy vegetables from selected markets in Lagos, Nigeria. Based on their persistence and cumulative

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behavior as well as the probability of potential toxicity effects, the absorption of heavy metals in human diets as a result of the consumption of vegetables and fruits means that there is a requirement for the analysis of food items to ensure that the levels of trace heavy metals meet the agreed international standards.

This is particularly important for farm products from parts of the world where only limited data on the heavy metal content are available.

The present study was undertaken with the aim to investigate the concentration levels of some heavy metals (Pb, Cd, Cu, Zn, Fe, Cr, Sn, Co, Mn and Ni in some selected fruits, vegetables and leafy vegetables collected from 4 different central local markets of Giza governorate. Also, this work aimed to estimate the health risk of heavy metals intake through the consumption of different fruits and vegetables, by calculating of the Estimated Provisional Tolerable Weekly Intakes (EPTDI), using resulting monitoring data and comparing to the metals recommended PTWI recommended to each element by the joint FAO/WHO Expert Committee on Food Additives (JECFA).

Materials and Methods

Sampling

A total of 70 samples of different commodities (i.e. tomato, green beans, potato, Molokai, strawberry, orange, and pomegranate) were purchased from several local markets of Giza governorates. The sampling comprised 2 kg for each commodity, which was considered to be quite representative for the analysis, only the edible portions of each fruit and vegetable were included, and additionally the bruised or rotten parts were removed.

Apparatus and Instruments

Milestone High-pressure microwave oven for samples Digestion, (Model: Ethos Up) purchased from Milestone – Italy. Water Purification System equipped with Q-POD® Element coupled with Merck Millipore – Q® integral 5 (A10®) / Model: ZRXQ005T0 - USA, the water delivered by the system have a resistivity of 18.2 M&!.cm at 25^{0}C, and conductivity of 0.055 micro Siemens. A Perkin Elmer Inductively coupled plasma optical emission spectrometer (ICP OES) Optima 8300 coupled with ultrasonic nebulizer U5000 AT + (CETAC), air compressor, autosampler S10, Meinhard nebulizer concentric glass K1- A3, quartz torch with copper foil, Polyscience whisper cools – USA, and gas supply for liquid argon of high purity. Plasma flow (12 L/min), nebulizer flow (0.35 L/min), auxiliary flow (0.2 L/min), RF power (1400 Watt), pump flow rate (2.5 L/min), view distance (15 cm), axial plasma view and the basic wavelengths for Cr, Co, Fe, Ni, Zn, Sn, Mn, Cu, Cd and Pb were (205.56, 230.786, 238.204, 227.02, 202.548, 189.927, 257.61, 327.393, 214.44, 206.836 and 220.353 nm) respectively. Mettler Toledo Top bench balance has ranged from 0.1 mg to 210g. Variable Micropipette (20-200µL) was purchased from Hirschman® Laborgerate - Germany.

Reagents

Concentrated Nitric acid (HNO_3) 65 % (w/w) was purchased from Merck - Germany. Emsure® Hydrogen peroxide (H_2O_2) 30 % was purchased from Merck - Germany. Certified Standard reference metals stock solutions (1000 mg/L) of Pb, Cd, Cu, Zn, Fe, Cr, Sn, Co, Mn, Lu, and Ni prepared in 2% HNO_3 were purchased from Merck- Germany.

Standard preparation

For intermediate standard solution (100, 10, 1 and 0.1 mg/L) of Pb, Cd, Cu, Zn, Fe, Cr, Sn, Co, Mn and Ni were prepared using 2% HNO_3. Nine working standard solutions, covering a range of 0.05-6 mg/L for Cu, Zn, Fe, Sn, Mn, Cr, Co and Ni. while eight working standard solutions, covering a range 1-100 µg/L for Cd and Pb. All working Standards were prepared by diluting suitable amounts of intermediate standard solution (100, 10, 1 and 0.1 mg/L) by 2% HNO_3.

Sample Preparation

According to the method described by Ghuniem *et al.*, 2019 homogenize the sample, weigh up to (1 g) of fruits or vegetables samples into the microwave digestion vessel. Add 8 mL of concentrated nitric acid to the digestion vessel and shake gently and wait for 30 minutes then add 2 mL of hydrogen peroxide. Seal the vessel carefully according to the manual instructions and place it in its holder in the microwave oven. Insert the thermocouple probe in the reference vessel and close the door. Adjust the microwave program as (Power = 1800 watt for 15 minutes until temperature reach 200^{0}C then let the temperature at 200^{0}C for 15 minutes, finally allow the microwave venting (Power = zero) until temperature < 80^{0}C). After microwave program has been completed, remove the thermocouple probe from the reference vessel to allow the vessels to cool down in a water bath for about 30 min then open the vessels carefully. Rinse down the lid and the walls with deionised water inside the vessel. Transfer the residual solution in 50 ml volumetric flask then add 0.2 ml from internal standard solution Lu (100 mg/L) and completed it with deionised water to the marked volume. The same procedure has to be followed for the reagent blank. The sample should be stored in polypropylene tubes until measured by ICP OES.

Analysis and Determination

First, a complete examination of all device connections as well as all of the conduction tubes is performed then performing the Mercury realignment to optimize the optical lenses and preference manganese test (1 mg/L) was used for axial viewing is useful to make sure all connection, nebulization and sensitivity are in good condition. All the standard solutions for tested elements (1000 mg/L) were used to prepare required concentrations (intermediate solutions) with UHQ (Ultra High Quality) water for preparation. The technique is based on the digestion solution was diluted to 50 ml with de-ionized water, then, the resulting solution was nebulized into core of coupled argon plasma that has 10,000 K temperature. The solution is then vaporized and the elements were automated, ionized and thermally excited and then detected and quantitated with ICP OES. Finally all measurements were converted to elemental concentrations by comparing it with calibration standards curve.

Quality assurance

The performance data of ICP OES methods in fruits and vegetables samples are presented in Table 2. The ICP OES method showed that a low levels of limit of quantifications (LOQs), which were varied between (0.02 – 1 mg/kg). The range of calibration curves were found to be (1, 3, 5, 10, 20, 40, 80 and 100 µg/l) for Cd and Pb, while the range of calibration curves were found to be (0.05, 0.1, 0.5, 1, 2, 3, 4, 5 and 6 mg/l) for Cr, Co, Cu, Fe, Mn, Ni, Zn and Sn. The linearity of the calibration curve based on the correlation coefficient, and all correlation coefficients were greater than 0.995. The method precision in the term of relative standard deviations (RSD%) were found to be ≤ 6.23%. The measurement uncertainty expressed as expanded uncertainty was found to be ≤ 23.76%.

Daily Intake of Heavy Metals through Fruits and Vegetables

The daily intake of heavy metals through the consumption of fruit and vegetables tested was calculated according to the equation Yu-Jing Cui *et al.*, 2004.

Daily intake of heavy metals (µg /day) = [Daily fruit or vegetable consumption × fruit or vegetable heavy metal concentration].

Results and Discussion

The present study reports on the heavy metal content of Pb, Cd, Cu, Zn, Fe, Cr, Sn, Co, Mn and Ni determined in some selected fruits, vegetables and leafy vegetables collected from 4 different central local markets of Giza governorate, Egypt. The mean concentrations and range of the investigated heavy metals found in fresh fruit and vegetables sampled from the local markets in Cairo and Giza governorates, are summarized in Tables from (3-9).

Chromium is the 17th most abundant element in earth mantle and naturally found as chromite in serpentine and ultramafic rocks or form complexes with other metals. Chromium is used in industrial applications, including industrial water cooling, paper pulp production, electroplating, tanning and petroleum refining, so hexavalent chromium in groundwater has generally been assumed to be anthropogenic contamination. The commonly existing oxidation states of chromium in the environment were Cr (III) and Cr (VI) because of their stability in the environment show amazingly contrasting properties. The Cr (III) is biologically essential for its role in sugar metabolism and protein, while Cr (VI) is considered potentially toxic and carcinogenic, and has an adverse impact on metabolic processes (Mandina et al., 2013, Rumpa *et al.*, 2011). In this study, the concentrations levels of Cr in orange, pomegranate, tomato and strawberry were found to be less than quantification limit ,while the concentration of chromium in potatoes, green beans and molokia were found to be ranged between (<1 - 1.1, <1 - 1.3 and <1 - 1.5) ppm respectively.

Cobalt is widely distributed in nature and its part of numerous anthropogenic activities. Cobalt is an important essential metal that is found in the active site of B12 vitamin and represents an important role in biochemical reactions of life. The sources of cobalt were allocated to four exposure settings: dietary, occupational, environmental and medical exposure. The main sources of the highest systemic cobalt concentrations inside the human body are oral intake of cobalt supplements and internal exposure. Excessive exposure has been shown to induce adverse health effects. Cobalt toxicology effects include vasodilation, flushing and cardiomyopathy in animals and human (Claudia *et al.,* 2017). In this study, the concentrations levels of Co in all commodities were found to be less than quantification limit.

Copper is one of the most important essential heavy metals found in all animals and food chain and environment, including water and soil and it's an essential nutrient for humans, animals and plants in small amounts. The biological functions of copper include normal iron metabolism, red blood cell synthesis, cell metabolism, connective tissue metabolism and bone development). The most important environmental sources of copper are in mining, smelting and refining of copper. Copper is found in all kinds of food but it's found in high concentration in organ meats, nuts, shellfish, beans and cocoa. Copper deficiency can cause anaemia, low numbers of white blood cells, osteoporosis in infants and children and also defects in connective tissue leading to skeletal problems. Acute toxicity to excessive intake copper can cause vomiting, temporary gastrointestinal distress with symptoms such as nausea and abdominal pain. Exposure to large doses of copper can cause Hepatic failure that resulted in death (Izah *et al.*, 2016, Mahurpawar 2015, Sevcikova *et al.*, 2011. In this study, the concentrations levels of Cu in orange, pomegranate, potatoes, tomato, green beans, strawberry and molokia were found to be ranged between (<1 - 1.9, <1 - 5.5, <1 - 3.5, <1 - 3.8, <1 - 2.5, <1 - 4.9 and 1.1 - 5.4) ppm respectively. The results also indicated that, 30% of analyzed molokia samples were found to be exceeded the maximum permissible limits in vegetables stated by Egyptian standards, while only 10 % of analyzed pomegranate samples were found to be exceeded the maximum permissible limits in fruits stated by Egyptian standards.

Iron is the fourth most abundant element which considered the most important part of the earth crust. Iron is essential element for almost every organism due to its involvement in all metabolic processes. Iron participates in a variety of functions in plants, animals and also microbes including electron transfer, hormone synthesis, substrate oxidation-reduction, oxygen transport and its storage, repair and cell cycle control, DNA replication, nitrogen fixation and protection from reactive oxygen species. Iron plays an important role in neuron signaling, as it's required for white matter of central nervous system in the brain and myelination of the spinal cord. Iron deficiency can cause many disease like anemia in human, While excess exposure to iron can cause several health implications such as an increased of heart diseases, cancer, diabetes, endocrine problems, arthritis and liver disease (Chitra *et al.*, 2017, Saini *et al.*, 2016, Ghuniem *et al.*, 2019. In this study, the concentrations levels of Fe in orange, pomegranate, potatoes, tomato, green beans, strawberry and molokia were found to be ranged between (1.7 - 9.4, 1.8 - 9.1, 33.2 - 681.5, 1.5 - 24.5, 11.4 - 64.7, 4.6 - 20.1 and 112.5 - 759.8) ppm respectively. The results also indicated that, All analyzed molokia and potatoes samples were found to be exceeded the maximum permissible limits in vegetables stated by Egyptian standards, 60% of analyzed green beans samples were found to be exceeded the maximum permissible limits in vegetables stated by Egyptian standards, 20% of analyzed strawberry samples were found to be exceeded the maximum permissible limits in vegetables stated by Egyptian standards, while only 10% of analyzed tomatoes samples were found to be exceeded the maximum permissible limits in vegetables stated by Egyptian standards.

Table 1: Microwave oven program.

Step no.	1	2	Venting
Power (watt)	1800	1800	0
Time(min.)	15	15	Until T1< 80o C
T1	200	200	< 80o C

Table 2: The results of method performance.

Elem ents	Practical LOQ (mg/kg)	Correl ation Coeffi cient	Reco very %	Preci sion (RSD %)	Expand ed unce rtainty (%)
Cr	1	0.9998	102.58	2.28	20.60%
Co	1	0.9998	98.47	2.41	20.66%
Cu	1	0.9998	101.27	3.30	21.23%
Fe	1	0.9998	97.54	6.23	23.76%
Mn	1	0.9994	107.65	2.21	20.57%
Ni	1	0.9996	92.57	2.69	20.82%
Zn	1	0.9997	110.78	4.76	22.34%
Sn	1	0.9997	101.96	2.90	20.93%
Cd	0.02	0.9999	107.39	4.08	21.74%
Pb	0.05	0.9997	96.35	3.69	21.44%

Manganese is the twelfth most abundant element in the earth crust and it's found naturally in water, food, soil and rocks. Manganese is considered heavy metal but it's important to biological system. Manganese plays an important role in living organism, including humans, such as oxidative phosphorylation, mucopoly saccharide metabolism, fatty acid and cholesterol metabolism and activation of some enzymes. The most food sources of manganese are cereals. Exposure to high concentrations of manganese causes toxicity to the central nervous, cardiac, respiratory and reproductive systems. The central nervous system (Brain and Spinal cord) is the sensitive target of exposure since toxic effects arise in this system at lower concentrations than in the other systems. Intake of Mn from drinking water may show significant risks for children's health, especially neurodevelopment (Santamaria, 2008, Lemos *et al.*, 2009). In this study, the concentrations levels of Mn in orange were found to be less than quantification limit while the concentration of Mn in pomegranate, potatoes, tomato, green beans, strawberry and molokia were found to be ranged between (<1 - 1.8, 1 - 14.4, <1 - 3.3, 2.1 - 3.7, 1.6 - 3.3 and 9.9 - 40.1) ppm respectively.

Nickel is one of trace elements widely distribute in the environment. Nickel is considered an essential micronutrient for many microorganisms and also for

Table 3: Metals contaminants in orange.

Total No. of Samples	Elements	Concentration			Frequency		MPL (mg/kg)	Violation Element		Violation Samples	
		Minimum	Maximum	Mean	No	%		No	%	No	%
10	Cr	<LOQ	<LOQ	1	9	90	-	-	-	0	0
	Co	<LOQ	<LOQ	1	7	70	-	-	-		
	Cu	<LOQ	1.9	1.2	8	80	5 Eg	0	0		
	Fe	1.7	9.4	4.04	10	100	15 Eg	0	0		
	Mn	<LOQ	<LOQ	1	10	100	-	-	-		
	Ni	<LOQ	<LOQ	1	8	80	-	-	-		
	Zn	<LOQ	1.8	1.11	10	100	5 Eg	0	0		
	Sn	<LOQ	<LOQ	1	9	90	-	-	-		
	Cd	<LOQ	<LOQ	0.02	3	30	0.05 Eu	0	0		
	Pb	<LOQ	0.05	0.05	2	20	0.1 Eu	0	0		

LOQ: Limit of quantification.
Eg: Egyptian standard.
Eu: European standard.

Table 4: Metals contaminants in pomegranate.

Total No. of Samples	Elements	Concentration			Frequency		MPL (mg/kg)	Violation Element		Violation Samples	
		Minimum	Maximum	Mean	No	%		No	%	No	%
10	Cr	<LOQ	<LOQ	1	7	70	-	-	-	2	20
	Co	<LOQ	<LOQ	1	8	80	-	-	-		
	Cu	<LOQ	5.5	1.98	9	90	5 Eg	1	10		
	Fe	1.8	9.1	4.76	10	100	15 Eg	0	0		
	Mn	<LOQ	1.8	1.34	10	100	-	-	-		
	Ni	<LOQ	1	1	8	80	-	-	-		
	Zn	1.2	3.6	2.73	10	100	5 Eg	0	0		
	Sn	<LOQ	<LOQ	1	10	100	-	-	-		
	Cd	<LOQ	<LOQ	0.02	7	70	0.05 Eu	0	0		
	Pb	<LOQ	0.12	0.08	3	30	0.1 Eu	1	10		

LOQ: Limit of quantification.
Eg: Egyptian standard.
Eu: European standard.

plants in low concentration but high concentration is toxic for human health. Nickel is present in the air, water and soil in deferent form. The most sources of Ni in food are cereals, fish, oils, canned food, dairy products, vitamin supplements and dried fruits. Workers in factories that exposure to Ni should elevated levels of nickel in blood, urine and body tissues (Aleksandra *et al.*, 2008, Pizzutelli, 2011). In this study, the concentrations levels of Ni in orange were found to be less than quantification limit while the concentration of Ni in pomegranate, potatoes, tomato, green beans, strawberry and molokia were found to be ranged between (<1 - 1, <1 - 3.2, <1 - 1.4, <1 - 5.6, >1 - 3.4 and >1 - 2.3) ppm respectively.

Zinc is considered essential trace element found in most kinds of food and may found in water in form of salts or organic complexes. Fish, meats, cereals, poultry and dairy are the highest food sources of zinc. Exposure to high level of zinc can cause serious toxicity to human health as well as to the ecosystem, therefore, zinc is considered as both an essential element and also toxic metal**.** Oral dose from zinc supplement can reduce the effects of the common cold; however, there is strong clinical researches that provide evidence that intranasal zinc gluconate gel treatment for this purpose could causes anosmia or the loss of the sense of smell among people who had used intranasal zinc sprays and gels(Anna and Samir, 2012, Huan *et al.*, 2016, Heidi *et al.*, 2016). In this study, the concentrations levels of Zn in orange, pomegranate, potatoes, tomato, green beans, strawberry and molokia were found to be ranged between (<1 - 1.8, 1.2 - 3.6, 2.2 - 492.9, <1 - 4, 2.7 - 7.9, <1 - 108.9, 3.3 - 11.6) ppm respectively. The results also indicated that, 60% of analyzed molokia samples were found to be exceeded the maximum permissible limits in vegetables stated by Egyptian standards, 30% of analyzed Potatoes samples were found to be exceeded the maximum

Table 5: Metals contaminants in potatoes.

Total No. of Samples	Ele ments	Concentration			Frequency		MPL (mg/kg)	Violation Element		Violation Samples	
		Minimum	Maximum	Mean	No	%		No	%	No	%
10	Cr	<LOQ	1.1	1.01	10	100	-	-	-	10	100
	Co	<LOQ	<LOQ	1	10	100	-	-	-		
	Cu	<LOQ	3.5	2.2	10	100	5 Eg	0	0		
	Fe	33.2	681.6	160.69	10	100	15 Eg	10	100		
	Mn	1	14.4	3.87	10	100	-	-	-		
	Ni	<LOQ	3.2	1.27	10	100	-	-	-		
	Zn	2.2	492.9	53.65	10	100	5 Eg	3	30		
	Sn	<LOQ	1	1	6	60	-	-	-		
	Cd	<LOQ	0.09	0.04	10	100	0.05 Eu	1	10		
	Pb	<LOQ	0.35	0.15	5	50	0.1 Eu	2	20		

LOQ: Limit of quantification.
Eg: Egyptian standard.
Eu: European standard.

Table 6: Metals contaminants in tomatoes.

Total No. of Samples	Ele ments	Concentration			Frequency		MPL (mg/kg)	Violation Element		Violation Samples	
		Minimum	Maximum	Mean	No	%		No	%	No	%
10	Cr	<LOQ	<LOQ	1	7	70	-	-	-	3	30
	Co	<LOQ	<LOQ	1	8	80	-	-	-		
	Cu	<LOQ	3.8	1.61	7	70	5 Eg	0	0		
	Fe	1.5	24.5	6.82	10	100	15 Eg	1	10		
	Mn	<LOQ	3.3	1.32	10	100	-	-	-		
	Ni	<LOQ	1.4	1.08	9	90	-	-	-		
	Zn	1	4	2.01	10	100	5 Eg	0	0		
	Sn	<LOQ	<LOQ	1	9	90	-	-	-		
	Cd	<LOQ	0.02	0.02	7	70	0.05 Eu	0	0		
	Pb	0.05	0.11	0.08	3	30	0.1 Eu	2	20		

LOQ: Limit of quantification.
Eg: Egyptian standard.
Eu: European standard.

permissible limits in vegetables stated by Egyptian standards, while only 20% of analyzed strawberry and green beans samples were found to be exceeded the maximum permissible limits in vegetables stated by Egyptian standards.

Tin is considered one of the toxic element, because of his ability to accumulation in human body and animals tissues. Tin may be released into the environment from manufacturing activity, windstorms, volcanic emission, forest fires, roads, and farming activities. The most commonly existing oxidation states of inorganic tin in environmental samples are Sn (II) and Sn (IV). Tin is used in tin-plated steel containers, which used for food production and preservation of beverage cans. Exposure to a high level of tin in canned food is taken daily over a long period, acute toxicity effects such as stomach aches, anaemia, occur problems in liver and kidney (Cima F., 2011, Ghuniem *et al.,* 2019). In this study, the concentrations levels of Sn in all commodities were found to be less than quantification limit.

Cadmium is found as an impurity in many products including fertilizers, pesticides, detergents and refined petroleum products. Some possible food sources of cadmium are found in peanuts, soybeans, rice, medicinal herbs, lettuce, corn, oats, wheat, spinach, fish, shrimps and mushroom. Exposure to cadmium at high levels can result in serious health problems related to bone defects in humans and also failure in liver and kidneys and can cause death (Andre *et al.,* 2005, Monisha *et al.,* 2014, Raja and Namburu 2014). In this study, the concentrations levels of Cd in orange, pomegranate and green beans were found to be less than quantification limit ,while the concentration of cadmium in potatoes, tomato, strawberry and molokia were found to be ranged between (<0.02 - 0.09, <0.02 - 0.02, <0.02 - 0.03 and 0.02 - 0.12) ppm respectively.

Table 7: Metals contaminants in green beans.

Total No. of Samples	Elements	Concentration			Frequency		MPL	Violation Element		Violation Samples	
		Minimum	Maximum	Mean	No	%	(mg/kg)	No	%	No	%
10	Cr	<LOQ	1.3	1.03	10	100	-	-	-	6	60
	Co	<LOQ	<LOQ	1	10	100	-	-	-		
	Cu	<LOQ	2.5	1.58	10	100	5 Eg	0	0		
	Fe	11.4	64.7	22.32	10	100	15 Eg	6	60		
	Mn	2.1	3.7	2.81	10	100	-	-	-		
	Ni	<LOQ	5.6	1.88	10	100	-	-	-		
	Zn	2.7	7.9	4.32	10	100	5 Eg	2	20		
	Sn	<LOQ	<LOQ	1	9	90	-	-	-		
	Cd	<LOQ	<LOQ	0.02	10	100	0.05 Eu	0	0		
	Pb	0.05	0.07	0.06	2	20	0.1 Eu	0	0		

LOQ: Limit of quantification.
Eg: Egyptian standard.
Eu: European standard.

Table 8: Metals contaminants in strawberry.

Total No. of Samples	Elements	Concentration			Frequency		MPL	Violation Element		Violation Samples	
		Minimum	Maximum	Mean	No	%	(mg/kg)	No	%	No	%
10	Cr	<LOQ	<LOQ	1	9	90	-	-	-	5	50
	Co	<LOQ	<LOQ	1	9	90	-	-	-		
	Cu	<LOQ	4.9	1.62	9	90	5 Eg	0	0		
	Fe	4.6	20.1	11.04	10	100	15 Eg	2	20		
	Mn	1.6	3.3	2.54	10	100	-	-	-		
	Ni	<LOQ	3.4	1.24	10	100	-	-	-		
	Zn	<LOQ	108.9	13.09	10	100	5 Eg	2	20		
	Sn	<LOQ	<LOQ	1	8	80	-	-	-		
	Cd	<LOQ	0.03	0.02	9	90	0.05 Eu	0	0		
	Pb	0.12	0.22	0.17	3	30	0.1 Eu	3	30		

LOQ: Limit of quantification.
Eg: Egyptian standard.
Eu: European standard.

Table 9: Metals contaminants in Molokia.

Total No. of Samples	Elements	Concentration			Frequency		MPL	Violation Element		Violation Samples	
		Minimum	Maximum	Mean	No	%	(mg/kg)	No	%	No	%
10	Cr	<LOQ	1.5	1.15	10	100	-	-	-	10	100
	Co	<LOQ	<LOQ	1	10	100	-	-	-		
	Cu	1.1	5.4	3.18	10	100	5 Eg	3	30		
	Fe	112.5	768	460.57	10	100	15 Eg	10	100		
	Mn	9.9	40.1	22.52	10	100	-	-	-		
	Ni	<LOQ	2.3	1.28	10	100	-	-	-		
	Zn	3.3	11.6	6.66	10	100	5 Eg	6	60		
	Sn	<LOQ	<LOQ	1	8	80	-	-	-		
	Cd	0.02	0.12	0.07	10	100	0.2 Eu	0	0		
	Pb	<LOQ	0.27	0.12	8	80	0.3 Eu	0	0		

LOQ: Limit of quantification.
Eg: Egyptian standard.
Eu: European standard

Lead has toxic effect in all humans and animals of all ages but the effects of lead are most serious in young children. The sources of lead exposure include mainly industrial processes, painting, mining, drinking water food and smoking (Sharma *et al.*, 2005 and Elgammal *et al.*, 2019). The main sources of Pb in different industrial

Table 11: Estimated daily intakes of tested elements (mg/kg b.w/day) from fruits and vegetables.

Commodity	Tested elements	concentration in mg/kg	Food consumption g/day	EPTDI mg/kg /day	EPTWI mg/kg bw/day	EPTWI mg/kg bw/week	APTWI mg/kg bw/week	EPTWI As a % of APTWI
Orange	Cu	1.20	38.0	0.0456	0.0008	0.0053	70	0.0076
	Fe	4.04	38.0	0.1535	0.0026	0.0179	315	0.0057
	Zn	1.11	38.0	0.0422	0.0007	0.0049	280	0.0018
	Pb	0.05	38.0	0.0019	0.0000	0.0002	0.025	0.8867
Pomegranate	Cu	1.98	113.4	0.2242	0.0037	0.0262	70	0.0374
	Fe	4.76	113.4	0.5398	0.0090	0.0630	315	0.0200
	Mn	1.34	113.4	0.1520	0.0025	0.0177	77	0.0230
	Ni	1.00	113.4	0.1134	0.0019	0.0132	7	0.1890
	Zn	2.73	113.4	0.3096	0.0052	0.0361	280	0.0129
	Pb	0.08	113.4	0.0094	0.0002	0.0011	0.025	4.3924
Potatoes	Cr	1.01	61.2	0.0618	0.0010	0.0072	-	-
	Cu	2.20	61.2	0.1346	0.0022	0.0157	70	0.0224
	Fe	160.69	61.2	9.8342	0.1639	1.1473	315	0.3642
	Mn	3.87	61.2	0.2368	0.0039	0.0276	77	0.0359
	Ni	1.27	61.2	0.0777	0.0013	0.0091	7	0.1295
	Zn	53.65	61.2	3.2834	0.0547	0.3831	280	0.1368
	Cd	0.04	61.2	0.0023	0.0000	0.0003	0.007	3.7740
	Pb	0.15	61.2	0.0093	0.0002	0.0011	0.025	4.3411
Tomato	Cu	1.61	102.8	0.1655	0.0028	0.0193	70	0.0276
	Fe	6.82	102.8	0.7011	0.0117	0.0818	315	0.0260
	Mn	1.32	102.8	0.1357	0.0023	0.0158	77	0.0206
	Ni	1.08	102.8	0.1110	0.0019	0.0130	7	0.1850
	Zn	2.01	102.8	0.2066	0.0034	0.0241	280	0.0086
	Cd	0.02	102.8	0.0021	0.0000	0.0002	0.007	3.4267
	Pb	0.09	102.8	0.0093	0.0002	0.0011	0.025	4.3176

products were battery, gasoline, solder in tin cans, water pipes and corrosion-resistant paints. From the major food commodities reported with high lead contamination were found in leafy vegetables, seafood, cereals, mineral salt, alcohol beverages and supplements. Exposure to lead cause many biological defects depending on the level and duration of exposure. Lead can cause serious injury to central nervous system brain, red blood cells and kidneys. Lead also breaks the blood-brain barrier and interferes with the normal development of the brain in infants (Mahmoud *et al.*, 2019, Maryse *et al.*, 2018). In this study, the concentrations levels of pb in orange, pomegranate, potatoes, tomato, green beans, strawberry and molokia were found to be ranged between (<0.05 - 0.05, <0.05 - 0.12, <0.05 - 0.35, 0.05 - 0.1, 0.05 - 0.07, 0.12 - 0.22 and <0.05 - 0.27) ppm respectively. The results also indicated that, 20% of analyzed potatoes and tomatoes samples were found to be exceeded the maximum permissible limits in vegetables stated by Egyptian standards, while only 10% of analyzed strawberry and pomegranates samples were found to be exceeded the maximum permissible limits in vegetables stated by Egyptian standards.

The higher levels of heavy metal contamination found in some fruit and vegetables could be closely related to the pollutants in irrigation water, farm soil, and pesticides or alternatively could be due to pollution from traffic on the highways Igwegbe *et al*., 1992.

Estimation of dietary intake

The results of the fruits and vegetables survey in combination with fruits and vegetables consumption data were taken into consideration to evaluate whether the estimated provisional tolerable daily intake (EPTDI) and estimated provisional tolerable weekly intake (EPTWI) of detected metals through each brand of fruits and vegetables consumed by the local Egyptian consumer was a cause of toxicological concern according to the recommended dose by the Food Agriculture Organization (FAO)/World Health Organization (WHO). The calculated (EPTDI) was obtained by multiplying the concentrations of metals detected and the amount of milk formula consumed. For essential elements, the estimated daily intakes (EPTDI) were compared to the metals

Table 11: Estimated daily intakes of tested elements (mg/kg b.w/day) from fruits and vegetables.

Commodity	Tested elements	concentration in mg/kg	Food consump tion g/day	EPTDI mg/kg /day	EPTWI mg/kg bw/day	EPTWI mg/kg bw/week	APTWI mg/kg bw/week	EPTWI As a % of APTWI
Green beans	Cr	1.03	7.5	0.0077	0.0001	0.0009	-	-
	Cu	1.58	7.5	0.0119	0.0002	0.0014	70	0.0020
	Fe	22.32	7.5	0.1674	0.0028	0.0195	315	0.0062
	Mn	2.81	7.5	0.0211	0.0004	0.0025	77	0.0032
	Ni	1.88	7.5	0.0141	0.0002	0.0016	7	0.0235
	Zn	4.32	7.5	0.0324	0.0005	0.0038	280	0.0014
	Pb	0.06	7.5	0.0005	0.0000	0.0001	0.025	0.2100
Strawberry	Cu	1.62	2.0	0.0032	0.0001	0.0004	70	0.0005
	Fe	11.04	2.0	0.0221	0.0004	0.0026	315	0.0008
	Mn	2.54	2.0	0.0051	0.0001	0.0006	77	0.0008
	Ni	1.24	2.0	0.0025	0.0000	0.0003	7	0.0041
	Zn	13.09	2.0	0.0262	0.0004	0.0031	280	0.0011
	Cd	0.02	2.0	0.0000	0.0000	0.0000	0.007	0.0700
	Pb	0.17	2.0	0.0003	0.0000	0.0000	0.025	0.1549
Molokia	Cr	1.15	9.7	0.0112	0.0002	0.0013	-	-
	Cu	3.18	9.7	0.0308	0.0005	0.0036	70	0.0051
	Fe	460.57	9.7	4.4675	0.0745	0.5212	315	0.1655
	Mn	22.52	9.7	0.2184	0.0036	0.0255	77	0.0331
	Ni	1.28	9.7	0.0124	0.0002	0.0014	7	0.0207
	Zn	6.66	9.7	0.0646	0.0011	0.0075	280	0.0027
	Cd	0.07	9.7	0.0007	0.0000	0.0001	0.007	1.1478
	Pb	0.12	9.7	0.0012	0.0000	0.0001	0.025	0.5387

Table 11: Ranges of elemental concentrations mg/kg in Fresh samples from present study and from other countries.

Elements	This study	Bangladesh	Algeria	China	Italy	United Kingdom
Cr	< 1 - 1.5	0. 32 - 0. 5	3 - 16.3	0.019 - 0.04		
Co	< 1					
Cu	< 1 - 5.5	0.95 - 6.82	3.8 - 29.5			
Fe	< 1.5 - 768					
Mn	< 1 - 40.1	10.75 - 13.75				
Ni	< 1 - 5.6	0.04 - 0.95		0.04 - 0.11		
Zn	< 1 - 492.9	0.24 - 0.57	11.2 - 49		4.9 - 42.9	
Sn	< 1					
Cd	< 0.02 - 0.12	0 - 0.04		0.001 - 0.004	0.009 - 0.37	1.8 - 123.4
Pb	< 0.05 - 0.35	0.003 - 0.011	12.3 - 39.3	0.009 - 0.027	0.07 - 3.3	4 - 529.4
References		Nazma *et al.*, 2016	Abdelhamid *et al.*, 2014	NIE et al., 2016	Eleonora *et al.*, 2013	Gareth *et al.*, 2015

recommended daily allowances (RDA) according to (Food and Nutrition Board, 2001). While for toxic elements, the long-term risk assessments of the intakes compared to the metals toxicological data were performed by calculating by dividing the (EPTWI) with the relevant acceptable provisional tolerable weekly intake (APTWI) set by (JECFA, 2005). In this study, the estimation of dietary exposure of metal, a consumption of rate of 2 – 113.4 g/person/day, depends on the commodity. Average weights of 60 kg were used for risk estimation.

The results showed that the intake of all elements didn't exceed the APTWI in all samples. The estimated exposure ranged from 0.0005% of the APTWI for copper (Cu) element in strawberry samples to 0.0343% of the APTWI for lead (Pb) element in potatoes samples See Table 10.

Table 11 compares the range of element concentrations in some fruit and vegetable samples found in our study and those from other countries. Observed Cr, Ni, Zn, Cd and Pb concentrations in our study were found to be higher than those of the concentration of Cr, Ni, Zn, Cd and Pb in fruit and vegetable samples from

Bangladesh Nazma *et al.,* 2016. Also the concentrations of Cr, Cu and Pb in our study were found to be lower than Cr, Cu and Pb concentrations in vegetable and fruit samples from Algeria Abdelhamid *et al.,* 2014. In other study the concentrations of Cr, Ni, Cd and Pb that found in some vegetable and fruit samples from China were lower than the concentrations of Cr, Ni, Cd and Pb in our study NIE *et al.,* 2016. It was reported that concentrations level of Cd and Pb in some vegetable and fruit samples from United Kingdom were be found higher than the concentrations of Cd and Pb in our study Gareth *et al.,* 2015.

Conclusion

In this study, microwave assisted digestion followed by analysis by ICP OES has been a simple and reliable methodology for the determination of some essential and toxic elements in fruits and vegetables. The study of seventy fruits and vegetables samples revealed that metal content strongly varied among of deferent samples varieties indicating that no standard compositional exists. Some metals as Co and Sn were found to be less than quantifications limits in all analysed samples. Overall, the estimated average daily intakes of essential elements below the recommended desired levels for essential metals. Also, toxic metals average weekly intakes were far below the provisional tolerable weekly intakes (PTWI). No health risk is expected from toxic metals from the consumption of these foods. This kind of studies would contribute to the identification of low-quality products on the market and assure a higher safety profile of fruits and vegetables.

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