Comparison Of the Content of Heavy Metals in Different Types of Local and Imported Oranges Collected from Market in the AL-zawia Region, Libya

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Abstract:
Despite the nutritional benefits obtained from orange consumption, the presence of heavy metals accompanying it from the environment draws scientific concerns as this affect human health. The aim of this study is to determine the content of lead (Pb), copper (Cu), iron (Fe), chromium (Cr), and manganese (Mn) in some selected oranges type (local, imported) from the Zawia City Market, Libya, were measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP – OES), the results of this study showed that the mean concentrations detected ranged from 1.74 ,4.27, 11.59, 0.155, 3.34, to 0.13, 0.53, 6.49, 0.06, 0.76 mg/kg, for Pb, Cu, Fe, Cr, and Mn, respectively. The highest mean level of Pb, Cr, and Mn were detected in oranges imported from Spain, Egypt and the highest mean level of Cu and Fe were detected in the local orange. In addition, the mean concentrations of metals in oranges (local, imported) collected from the Zawia City Market decrease in the following order: Fe > Cu > Mn > Pb > Cr. The levels of these metals found in our study were compared with the recommended limit as established by the FAO/WHO in 2001to assess the levels of food contamination.
Based on the observation in this study, there is need for continuity of heavy metals inspection in agricultural products in order to prevent contamination and secure human safety.
Keywords: heavy metal; types of oranges (local, imported); food safety; Inductively Coupled Plasma Optical Emission Spectroscopy (ICP – OES).

Introduction

The orange fruit is the most widely consumed fruit in the world, especially in subtropical areas. (Selli,2004) Almost all of it is grown in western Libya, and it is popular throughout the country. Minerals such as sodium, calcium, magnesium, copper, manganese, and iron are abundant in orange fruit. They also include a variety of vitamins, like A and C, which are antioxidants. Additionally, lowering cholesterol levels protects humans from heart disease (Rigby, 2011) by protecting cells from damage caused by free radicals. (Franke,2004) There are many different types of orange fruit, such as (sweet oranges, mandarin oranges, navel oranges, blood oranges, clementine or kumquat oranges). It has been discovered many imported oranges from Egypt, Tunisia, Spain, and China at local supermarkets.

Organic insecticides containing heavy metals such as lead, cadmium, zinc, and copper, as well as inorganic insecticides containing mercury, copper, lead, zinc, and arsenic, damage the agricultural soil. The major factors generating soil contamination around the world are treated wastewater and untreated water. Heavy metal's mobility in soil is influenced by its chemical form. The first reaction is absorption, which takes minutes to hours to be absorbed by the soil. And the second is adsorption reaction which takes days or even years to complete. Heavy metals are repurposed in a variety of chemical ways through their bioavailability. (Islam, 2001) Heavy metals are becoming more prevalent as a result of the reintroduction of chemical compounds into the soil and Irrigation with municipal trash and wastewater. The soil's quality is determined by Specifically, the degree of temporal and geographic variation in its physical, chemical, and biological features as a result of human and natural effects. (smit.H. 1997 & Schindelbeck, 2008).

Materials and methods

2. Materials and methods

2.1- Sampling

A total of (10) samples of different types of orange purchased from several local markets in Zawia City, Libya, during the period January to march 2021. The sampling comprised (1kg) for each commodity sold in each district were scattered randomly throughout the city, for the analysis, only the edible portions of each orange was included, and additionally the bruised or rotten parts were removed.

2.2- Sample identifications

Table (1) show the types of orang samples analyzed**Table (1)** show the types of orang samples analyzed

samples	types	Production /source	Number of samples
Sample1	tangerine / kenny	Local	3
Sample2	Navel / bosri	Local	3
Sample3	Blood orang	Local	3
Sample4	Clementine / kumquat	Local	3
Sample5	Sweet orang	Locale	3
Sample6	tangerine / kenny	Egyptian	3
Sample7	navel	Egyptian	3
Sample8	tangerine / kenny	Spanish	3
Sample9	tangerine / kenny	Tunisia	3
Sample10	navel	Tunisia	3

Sample preparation and treatment

2.3- Sample preparation and treatment

Sub -samples (1kg) each were taken at random from the composite sample (10kg) and were processed for analysis by the dry-a shing method. The samples were first oven dried at 105°C for 24 h. the dried samples were powdered in a mixer grinder and were subjected to analysis for their heave metal content. powdered samples (14gr), with three replicates taken for each orang item. Were accurately weighed and placed in silica crucible, and few drops of concentrated nitric acid were added to the solid as an aid to a shing. the dry -a shing process was carried out in a muffle furnace by stepwise increase of the temperature up to 550℃ and the samples left to ash at this temperature for 6 h (Crosby, 1997).

The ash was kept in desiccators and then rinsed with 3N Hydrochloric acid. the ash suspension was filtered into a50ml volumetric flask through Whatman No.1 filter paper, and the volume was made up to the mark with 3N Hydrochloric acid.

2.4- standards

A series of standard solutions for heavy metals, namely lead (Pb), copper (Cu), iron (Fe), chromium (Cr), and manganese (Mn), were prepared and measured, resulting in the calibration curves as shown in figure (1) with determination coefficients.

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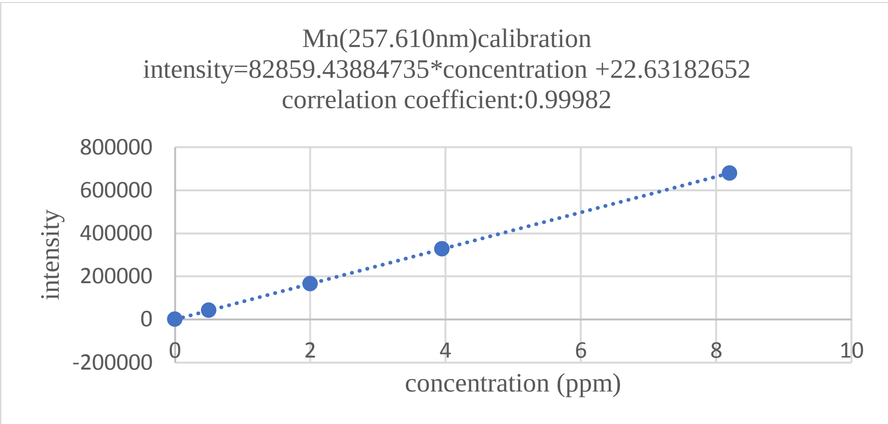
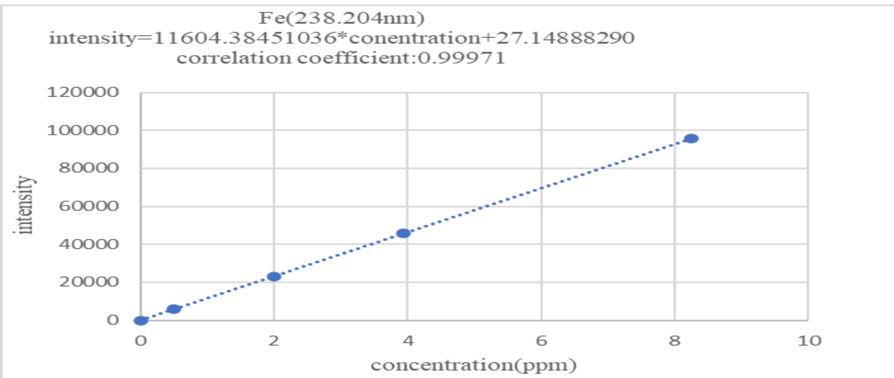




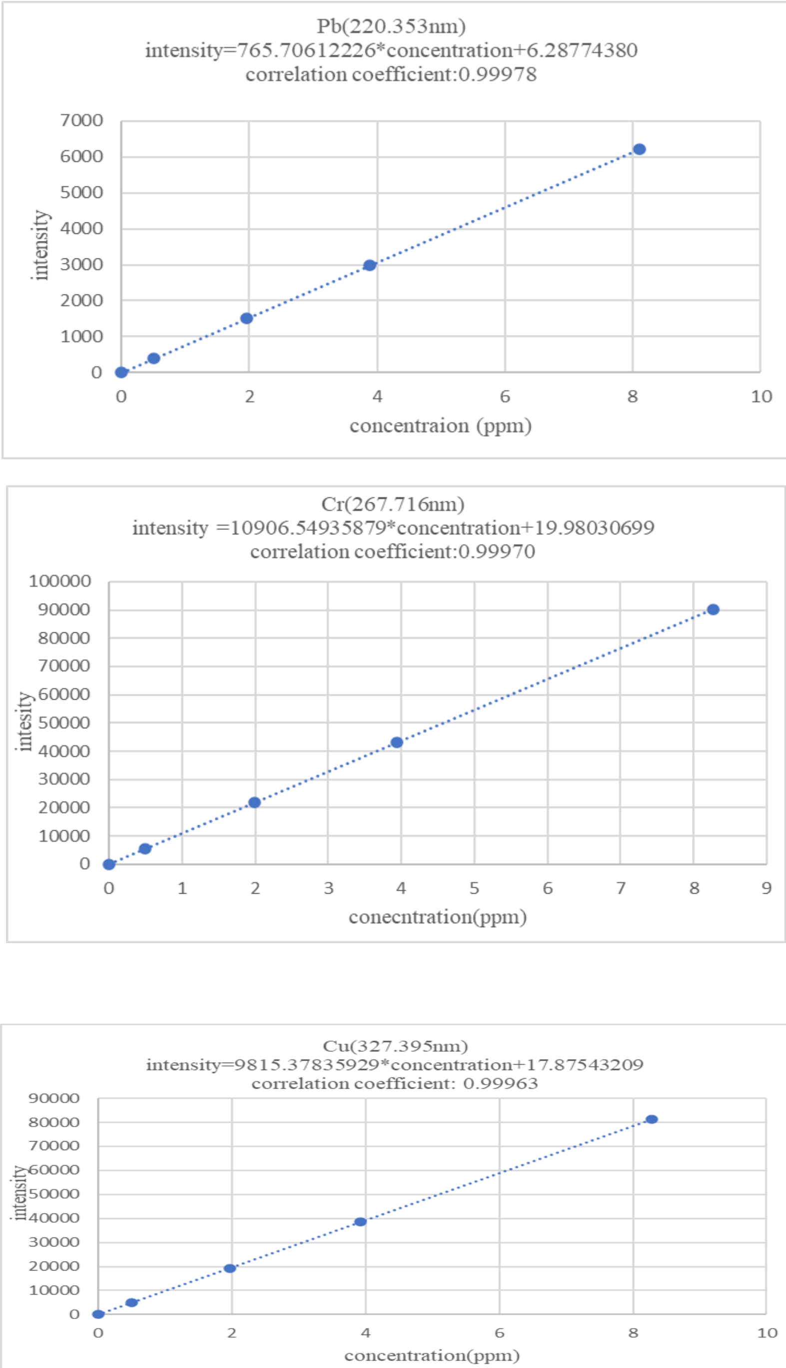


Figure (1) The calibration curves for heavy metals

Quality assurance:
Appropriate quality assurance procedures and precaution were taken to ensure the reliability of the results. samples were carefully handled to avoid cross contamination.

Glassware was properly cleaned, and reagent used were of analytical grades. distilled water was used throughout the study was supplied from Zawia electric station. Reagents blank determinations were used to correct the instrument reading. For validation of the analytical procedure, repeated analyses of the samples against a recovery study were carried out by spiking and homogenizing several already analyzed samples with varied amounts of standard solutions of the metals. The spiked samples were processed for analysis by the dry a shing method and reanalyzed as described above. The average recoveries obtained were 89.02%,95.9%,98.3%,91.36%, and 99.2% for Pb, Mn, Cr, Cu, and Fe, respectively.
Inductively Coupled Plasma Optical Emission Spectroscopy (ICP - OES)
Analysis for heavy metal of interest was performed using inductively coupled plasma optical emission spectroscopy [Agilent 5110 ICP-OES] at the laboratory of Libyan petroleum institute. the limit of detection (L.D) of the analytical method for each metal was calculated as double the standard deviation of a series of measurements of a solution, the concentration of which is distinctly detectable above the background level. These values were 0.002,0.03,0.002,0.005, and 0.0003 mg/L for Cu, Pb, Cr, Fe, and Mn, respectively. For the determination of these metals three solutions were prepared for each sample. The means of these figure were used to calculate the concentrations.
The standard operating conditions for the analysis of heavy metals using (ICP-OES) used in our experiments are given in table (2,3)

Table (2) ICP-OES instrument and method parameters

Parameter	**Setting**
Viewing mode	Radial
Viewing height(mm)	8
Read time(s)	5
RF power(kw)	1.2
Stabilization time (s)	15
Nebulizer flow(l/min)	0.7
Plasma flow(l/min)	12
Pump speed (rpm)	12
Sample introduction	Manual
Sample uptake time (s)	25
Replicates	3

Table (3) wavelength and working and calibration rang

Element	Wavelength(nm)	Background correction	Calibration fit
Fe	238.204	Fitted	Liner weighted
Cr	267.716	Fitted	Liner weighted
Mn	257.610	Fitted	Liner weighted
Pb	220.353	Fitted	Liner weighted
Cu	327.395	Fitted	Liner weighted

RESULTS AND DISCUSSION

The concentrations of heavy metals in the orange samples collected from Zawia City markets are shown in (Table 4) The values are given as mean ± SD and the results are means of three replicates.

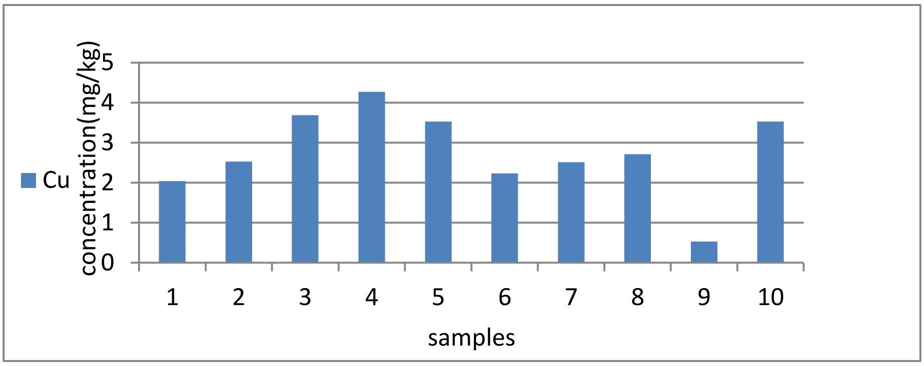
Table 4: Average concentration of Heavy Metals (SD, n = 3, mg/kg or ppm dry weight) in orange Collected from Zawia Market.(

Samples	Pb	Fe	Mn	Cr	Cu
Sample1	0.23±0.063	7.71±0.17	1.64±0.01	0.107±0.03	2.04±0.03
Sample2	0.13±0.036	6.49±0.01	0.76±0.01	0.107±0.03	2.53±0.08
Sample3	0.14±0.080	11.59±0.29	1.32±0.01	0.107±0.03	3.69±0.07
Sample4	0.13±0.036	9.74±0.02	1.59±0.02	0.119±0.03	4.27±0.02
Sample5	0.17±0.046	9.21±0.10	$2.14\pm8.16\times10^{-3}$	0.08±0.02	3.53±0.08
Sample6	1.49±0.042	9.55±0.06	$1.9\pm5.77\times10^{-3}$	0.155±0.04	2.23±0.11
Sample7	0.36±0.060	8.75±0.38	$1.56\pm6.08\times10^{-3}$	0.08±0.02	2.51±0.11
Sample8	0.14±0.040	8.75±0.19	3.12±0.02	0.07±0.02	2.71±0.01
Sample9	1.74±0.490	10.31±0.12	3.43±0.01	0.07±0.02	0.53±0.02
Sample10	0.18±0.050	8.78±0.51	$1.33\pm7.07\times10^{-3}$	0.06±0.01	3.53±0.2
WHO/FAO (mg/Kg)	0.5	1	5	0.5	2

From the results obtained, it was shown that:

Copper (Cu):

Copper is an essential trace element required for proper health in an appropriate limit. Its high intake in fruits can be harmful for human health and in the same way; low intake can cause a number of symptoms like growth retardation, skin ailments, and gastrointestinal disorders (Kalagbor, 2014). As can be from Table 4, the concentration of copper ranged from 0.53–4.27 mg/kg in orange samples collected from Zawia market. The highest and the lowest concentration of Cu were accumulated by sample no.4 (4.27 mg/kg) and sample no.9 (0.53 mg/kg) respectively. As can be seen from Table4. The FAO/WHO maximum limit for Cu concentration in fruits is 2mg/kg. The result obtained in this(WHO, 2001) study is higher than the recommended limit



in all samples expected sample no.1and no. 9.

Figure (2) Concentration of Cu in orange fruits.

Iron (Fe):

Iron is a necessary metal and is a core component of red blood cells, its deficiency can cause anemia (Ismail1,2001). Results showed that Fe was accumulated most among the samples analyzed for heavy metals levels. The maximum concentration of iron was found in sample no.3(11.59 mg/kg) and the minimum in sample no.2(6.49 mg/kg) in samples collected from Zawia market Table 4. The FAO/WHO (WHO, 2001). maximum limit for Fe concentration in oranges is 1 mg/kg. The result obtained in this study is higher than the recommended limit in all samples.

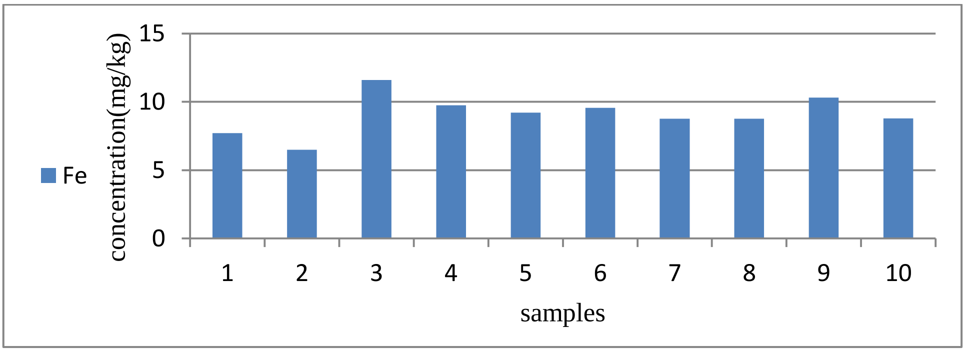
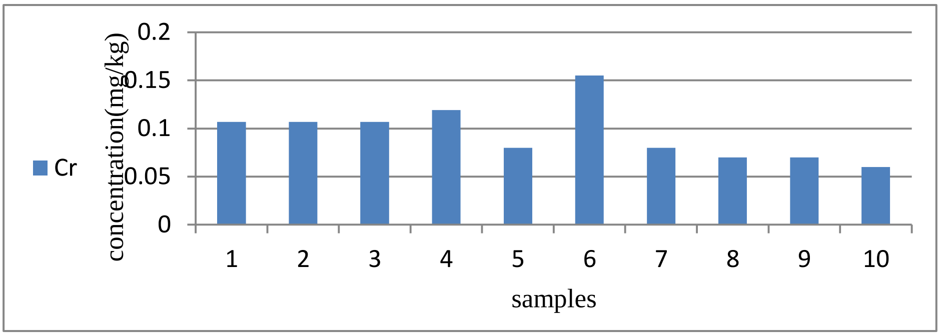


Figure (3) Concentration of Fe in orange fruits.

Chromium (Cr):

Chromium particularly Cr (III) plays an important role in the body function in trace amount but it is toxic in excess amount. However, Cr (VI) is toxic and has no role in body (Mubeen, 2009). The maximum concentration of Chromium was found in sample no.6 (0.155 mg/kg) and the minimum in sample no.10 (0.06 mg/kg) in samples collected from Zawia market Table 4. These value s are lower than the maximum permissible limit of 0.5 mg/kg by FAO/WHO (Saraf,2013) The toxic effects of Cr intake are skin rash, nasal irritation, itching and bleeding, stomach upset, kidney and liver damage, and lungs cancer. Chromium deficiency is characterized by disturbance



of glucose, lipids and protein metabolism (Khan,2008).

Concentration of Cr in orange fruits **Figure (4)**

Manganese (Mn):

Manganese is essential for the normal bone structure, reproduction. It plays a very essential role in the functioning of the central nervous system. Mn deficiency will lead to failure of reproduction in both males and females (Saraf,2013) . Mn showed maximum concentration in sample no.9 (3.43 mg/kg) and the minimum in sample no.2 (0.76 mg/kg) in samples collected from Zawia market Table 4. The content of Mn reported in this study was generally lower than the permissible levels 5.0mg/kg set by FAO/WHO (WHO, 2001) in oranges.

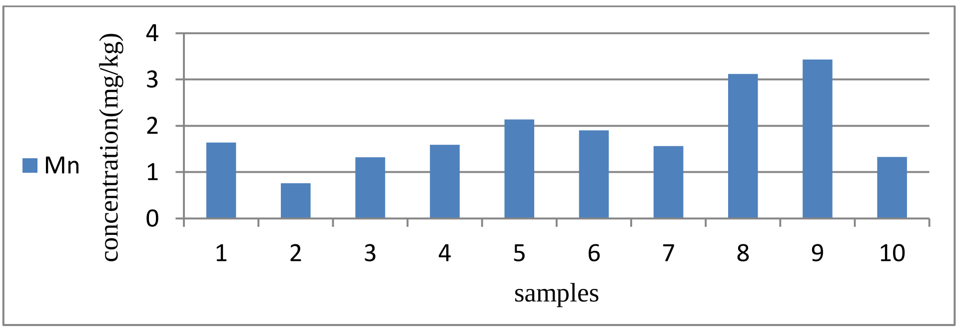


Figure (5) Concentration of Mn in orange fruits.

Lead (Pb):

Lead is a serious cumulative body poison which enters into the body system through the air, water and food and cannot be removed by washing fruits (Divrikli, 2006). Results obtained showed that the concentration of Pb showed maximum concentration in sample no.9 (1.74 mg/kg) and the minimum in sample no.2 and no. 4 (0.13 mg/kg) in samples collected from Zawia market Table 4. The content of Pb reported in this study was generally lower than the permissible levels set by FAO/WHO (WHO, 2001) in oranges expected sample no.6 and no. 9.

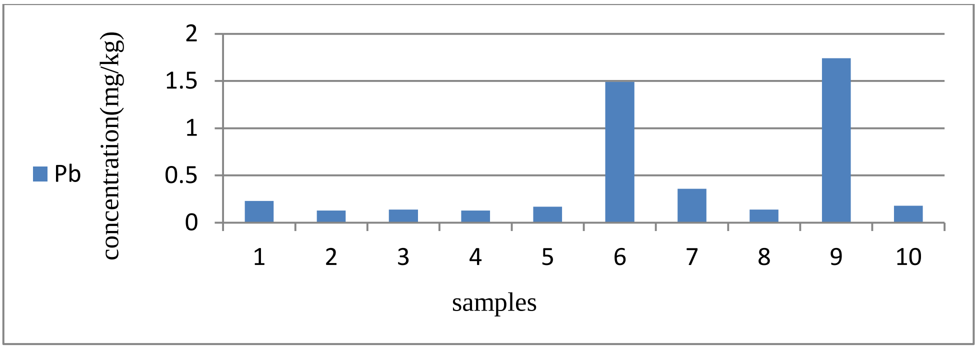


Figure (6) Concentration of Pb in orange fruits.

For the average concentration of these elements in the local and imported orange samples, they were as described in Tabel (5)

sources	Concentration of heavy metals (mg/kg)				
	Pb	**Fe**	**Mn**	**Cr**	**Cu**
Imported	0.782	9.228	2.268	0.087	2.302
Local	0.16	8.95	1.49	0.104	3.212

As these results showed that the average concentrations of Pb, Fe, and Mn in imported orange samples were higher than the local orange samples, while the average concentration of both Cu, and Cr were higher in local orange samples than imported orange samples.

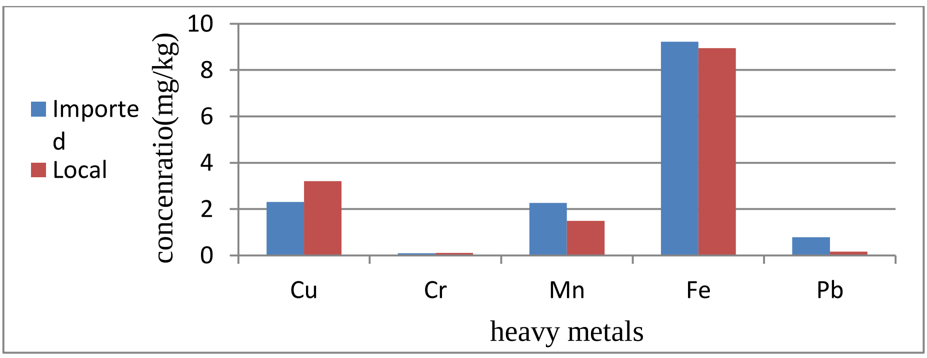


Figure (7) the average concentration of elements in the local and imported orange samples

When comparing the concentration of heavy elements in one of the (mandarin oranges) from different sources (Libya, Egypt, Tunis, Spain), it was found that the highest concentration of lead, iron and manganese was in the Tunisian mandarin and the highest concentration of copper was in the Spanish mandarin whereas, the highest concentration of chromium was in the Egyptian mandarin. The highest concentrations of all elements were found in the imported samples.

Table(6) comparing the concentration of heavy elements in the (mandarin oranges) from different sources (Libyan, Egyptian, Tunisian, Spanish)

sources	Concentration of heavy metals (mg/kg)				
	Pb	**Fe**	**Mn**	**Cr**	**Cu**
mandarin Libyan	0.23	7.71	1.64	0.107	1.95
mandarin Egyptian	1.49	9.55	1.9	0.155	2.52
mandarin Tunisian	1.74	10.31	3.43	0.07	0.58
mandarin Spanish	0.14	8.75	3.12	0.07	2.68

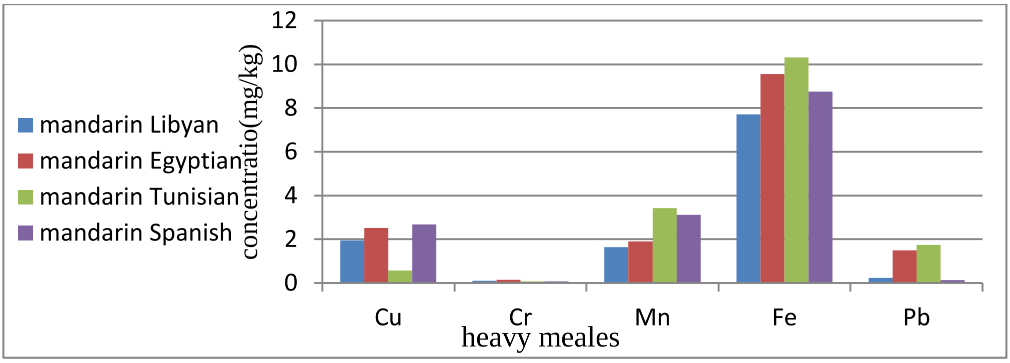


Figure (8)comparing the concentration of heavy elements in the (mandarin oranges) from different sources (Libyan, Egyptian, Tunisian, Spanish)

However, (imported orange samples) had higher concentration of heavy metals than (local orange samples). The main reason for the relatively high level of heavy metals in those samples (imported orange samples) is the samples come from different regions of the country, where the sources production of the fruits is unknown and the other reason may be contamination at the time of transportation. In general, the results indicate that the order of the concentration of heavy metals in orange samples, (imported orange samples) were found to follow decreasing order: Fe > Cu > Mn >Pb > Cr and the concentration of heavy metals in orange samples, (local orange samples) were found to follow decreasing order: Fe > Cu >Mn > Pb > Cr. When the present concentrations of heavy metals were compared with the permissible limits by FAO/WHO, it was found out that all the levels of Cr and Mn were within the safe limit. As for lead concentration, it exceeded the permissible limit in sample no. 9 and no. 6, and copper concentrations exceeded the permissible limit in sample no. 9 and no.1, while iron concentrations exceeded the permissible limit in all samples.

The high levels of heavy metals found in some samples might also be closely related to the pollutants found in irrigation water, farm soil or due to pollution from the highways traffic. Furthermore, Agronomic practices such as the application of fertilizer, pesticides and water managements on growing these samples could be affecting the accumulation of these heavy metals.

CONCLUSION

Heavy metals were estimated in oranges collected from Zawia City Market, Libya. The results obtained revealed that there is a relatively higher concentration of heavy metals in orange samples procured from Egypt, Tunisia, and Spain than local orange samples while Chromium (Cr) and Manganese (Mn) concentrations in both were below the detection limit. However, Heavy metals have a toxic impact, but detrimental impacts become apparent only when long term consumption of contaminated orange occurs. It is therefore suggested that regular monitoring of heavy metals in orange and other food items should be performed in order to prevent excessive buildup of these heavy metals in the human food chain. Appropriate precautions should also be taken at the time of transportation and marketing of oranges.

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الملخص:

على الرغم من الفوائد الغذائية التي يتم الحصول عليها من تناول البرتقال، الا أن وجود المعادن الثقيلة المصاحبة له من البيئة يثير بعض المخاوف لان هذا يؤثر على صحة الانسان. الهدف من هذه الدراسة هو تحديد محتوى الرصاص (Pb)، النحاس (Cu)، الحديد (Fe)، الكروم (Cr) والمنجنيز (Mn) في بعض أنواع البرتقال (المحلي، المستورد) التي تم جمعها من أسواق مدينة الزاوية، باستخدام تقنية التحليل الطيفي للانبعاثات الضوئية لبلازما الحث المزدوج (ICP – OES)، حيث أظهرت نتائج هذه الدراسات ان متوسط التراكيز المقاسة تراوحت من (3.34،0.155،11.59،4.27،1.74، الى 0.13،0.58،0.06،6.49، 0.76 مجم / كجم) للرصاص، النحاس، الحديد، الكروم، والمنجنيز على التوالي. حيث كان متوسط اعلى مستوى للرصاص والكروم والمنجنيز في البرتقال المستورد من اسبانيا ومصر، وكان متوسط اعلى مستوى للنحاس والحديد في البرتقال المحلي، وبالإضافة الى ذلك يقل متوسط تركيز المعادن في البرتقال (المحلي والمستورد) الذي تم جمعه من أسواق مدينة الزاوية حسب الترتيب التالي (Fe> Cu > Mn > Pb > Cr). وتمت مقارنة مستويات المعادن المدروسة مع الحد الموصي به على النحو الذي حددته منظمة الأغذية والزراعة / منظمة الصحة العالمية في سنة 2001 لتقييم مستويات تلوث الأغذية.

وبناء على الملاحظات في هذه الدراسة، تبين ان هناك حاجة لاستمرار فحص المعادن الثقيلة في المنتجات الزراعية من أجل منع التلوث وتأمين سلامة الانسان.