ISSN 2063-5346

A COMPARISON OF THE CONCENTRATIONS OF SOME HEAVY METALS IN SOME WASHED AND UNWASHED FRUITS COLLECTED FROM THE MARKETS OF AL-ZAWIYA CITY

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Article History: Received: 01.02.2023 **Revised:** 07.03.2023 **Accepted:** 10.04.2023

Abstract

This study was conducted to determine the concentration of four heavy metals (Cr, Cu, Ni, , and Pb) in some washed and unwashed fruits namely: Strawberries, Apricot, peache, Apple, and plum collected from Azawia markets. Dry ashing method was used for the digestion of samples. The heavy metals were analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP – OES). The results obtained showed that the concentrations of heavy metals in washed fruits ranged from 0.036–0.214, 0.571–3.106, 0.071–0.339, and 0.107–0.750 mg/kg for Cr, Cu, Ni, and Pb respectively. In unwashed fruits the concentrations of Cr, Cu, Cr, and Pb ranged from 0.071–0.571, 0.975–3.749, 0.125–0.678, and 0.250–2. 035 mg/kg respectively.. In addition, the mean concentrations of metals in the washed fruits decreases in the following order: Cu > Pb> Ni >Cr and for unwashed fruits decreases in the following order: Cu > Pb> Ni >Cr . The levels of Ni and Cr were all below the permissible limits set by FAO/WHO in washed fruits,While the concentration of lead was higher than the permissible limit in washed and unwashed strawberry fruits and unwashed peaches and apples. The copper concentration level was higher than the permissible limit in all samples.

Keywords: Heavy metals, washed and unwashed fruits, food safety, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP – OES).

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DOI: 10.31838/ecb/2023.12.s1.128

1.Introduction

A major societal concern on a global scale is food safety. Recent decades have seen a rise in research on the risks associated with consuming food products contaminated with pesticides, heavy metals, or poisons. **[Singh et al.,2010; Nabulo et al.,2011].** Fruits are very important in the diet since they contain vitamins, water, dietary fiber and mineral salt. They are crucial protective foods that are beneficial for maintaining human health **[D'Mello JPE 2003].** A regular consumption of fresh fruits, such as apples, plums, peaches, apricots, and strawberries, is essential for supplying human body with the nutrients they require for continued growth and vigor [**Mausi et al., 2014**].

on the other hand, these plants have a wide range of essential and hazardous metal concentrations. According to reports, heavy metals can play both beneficial and harmful functions in a human life **[Adriano DC (1984)].** Some heavy metals such as cadmium, and lead are major contaminants of food, supply and may be considered the most important problem to our environment, while others like iron, zinc and copper are essential for biochemical reactions in the body **[Zaidi MI., 2005].** The majority of heavy metals are typically not biodegradable, have lengthy biological half-lives, and have the potential to accumulate in various human organs, causing undesirable side effects **[Jarup L 2003, Sathawara NG 2004].**

Fruits absorb heavy metals via airborne deposits on plant sections exposed to the air from polluted settings, over and above, from contaminated soils through root systems, and also if they are watered with tainted water **[M.S Al Jassir A 2005].** Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES) is one of the analytical techniques that used to determine how much of certain heavy metals are in a fruit samples.

The present study was carried out in order to compare and investigate the concentration of some specific heavy metals (Cr, Cu, Ni, and Pb) found in some washed and unwashed selected fruit from this region since it is unknown whether fruits from Al zawia city – Libya are contaminated with heavy metals.

. Material and Methods2

2.1. Sample collection. A total of five kinds of fruit(Strawberries, Peache, Apricot, Apple, Plum) produce were purchased from several local supplies and markets in Zawia City, Libya, during 2021 from march to June. The sampling comprised 3Kg for each commodity sold in each district were scattered randomly throughout the city; for the analysis, only the edible portions of each fruit was included, and additionally the bruised or rotten parts were removed, the edible potions of each fruit were randomly divided into two fractions. the first fraction was soaked in tap water for 15 min to remove the pesticides and impurities, and then washed twice with distilled water, decant the water present on it, then soaked one more time for 15 min by distilled water, and the sample labeled as washed sample, the second fraction was subjected to digestion without washing and hence labeled as unwashed sample, the figure (1) shows the stages of washing and soaking some fruits.

Figure (1) the stages of washing and soaking some fruits

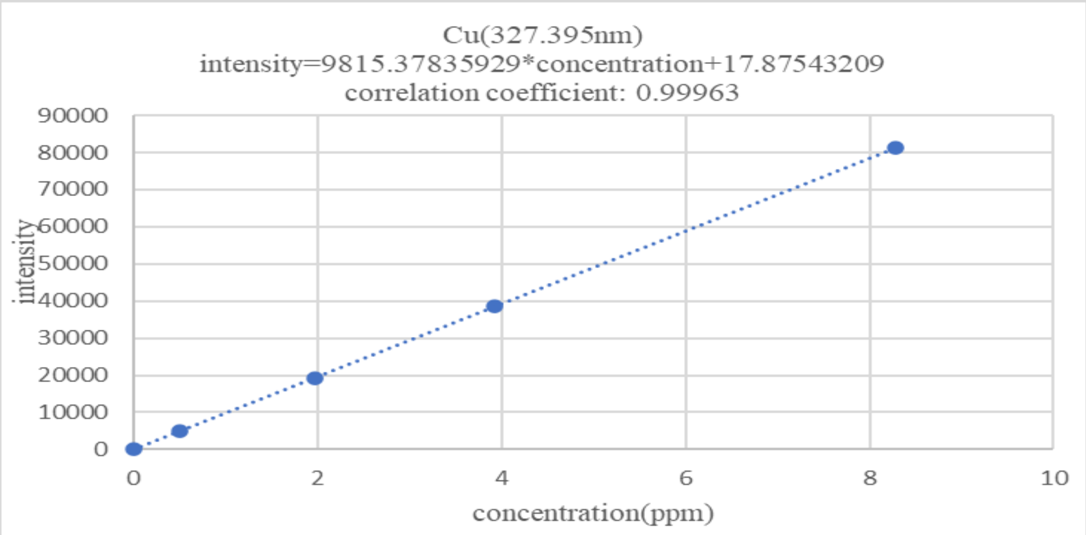
2.2. Sample Preparation and Treatment.

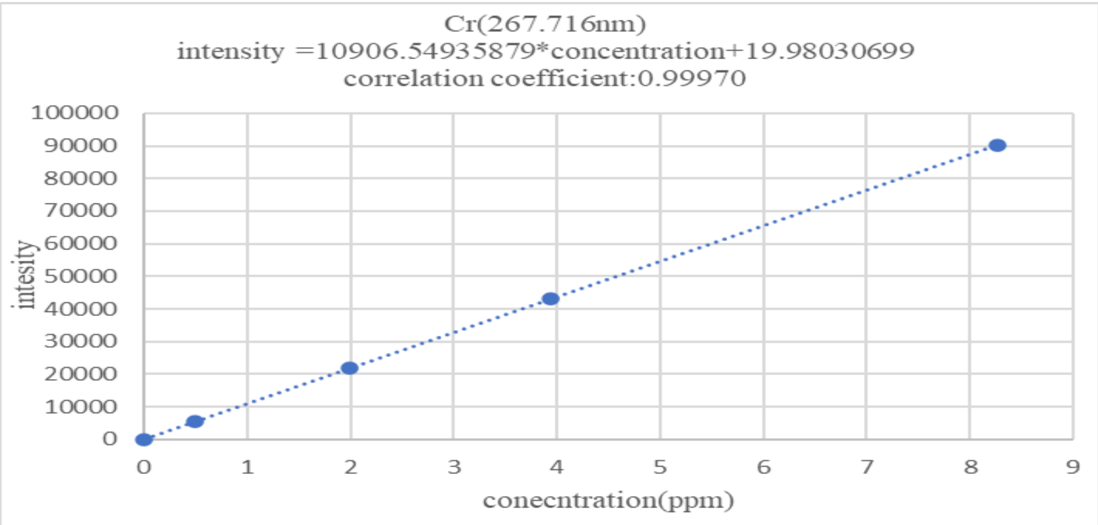
Both the washed and unwashed samples were processed for analysis by the dry-a shing method. The samples were first oven dried at 105°C for 24 h. the dried samples were powdered in a mixer grinder and were subjected to analysis for their heave metal content. powdered samples (14gr), with three replicates taken for each fruit. 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°C and the samples left to ash at this temperature for 6 h **[Crosby, 1997].**

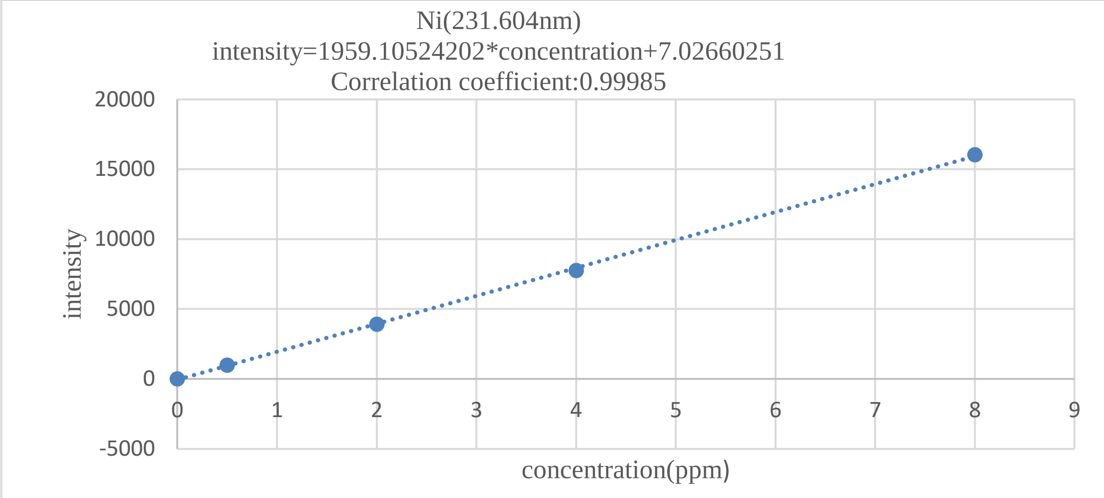
The ash was kept in desiccators and then rinsed with 3N Hydrochloric acid. the ash suspension was filtered into a50ml volumetric flask through Whatman No.1 filter paper, and the volume was made up to the mark with 3N Hydrochloric acid.

2.4- standards

A series of standard solutions for heavy metals, namely chromium (Cr), copper (Cu), Nickel (Ni), and Lead (Pb), were prepared and measured, resulting in the calibration curves as shown in figure (2) with determination coefficients.







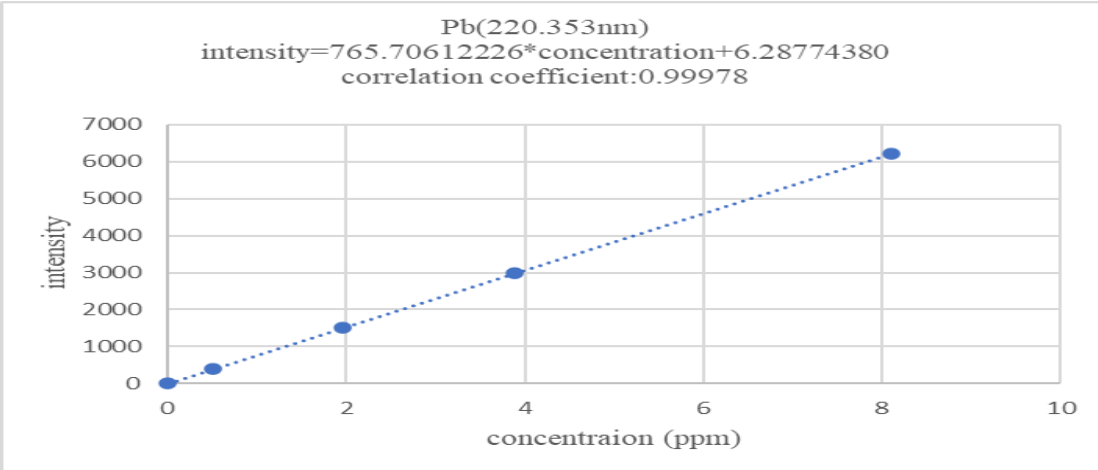


Figure2:the calibration curves forheavy metals

2.5- 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 98.3%, 91.36%,67,and 89.02% for Cr, Cu, Ni, and Pb respectively.

2.6- 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 0.002,0.002,0.01, and

0.003 mg/L for Cr, Cu, Ni, and Pb, 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 (1,2)

Table (1) 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 (2) wavelength and working and calibration ran

Element	**Wavelength(nm)**	**Background correction**	**Calibration fit**
Cr	267.716	Fitted	Liner weighted
Cu	327.395	Fitted	Liner weighted
Ni	231.604	Fitted	Liner weighted
Pb	220.353	Fitted	Liner weighted

3. Results and discussion

The mean concentration of heavy metals in the unwashed and washed fruit samples are presented in Table 3.

Table3: Mean ±S.D (mg/kg)) of metals in the unwashed and washed some fruits

Sample types	Samples	Cr	Cu	Ni	Pb
Strawberries	Washed	$0.214\pm5.97\times10^{-3}$	0.893±0.054	0.143±0.000	0.750±0.040
	Unwashed	0.571±0.140	2.035±0.187	$0.179\pm4.76\times10^{-3}$	2.035±0.187
Peache	Washed	0.143±0.000	0.797±0.040	0.321±0.034	0.232±0.0771
	Unwashed	$0.179\pm4.76\times10^{-3}$	3.749±0.012	0.678±0.000	0.809±0.054
Apricot	Washed	0.071±0.126	0.928±0.590	0.339±0.021	0.107±0.010
	Unwashed	$0.143\pm4.76\times10^{-3}$	2.214±0.187	$0.464\pm9.43\times10^{-3}$	0.450±0.031
Apple	Washed	$0.036\pm1.73\times10^{-3}$	3.106±0.099	$0.214\pm5.97\times10^{-3}$	0.238±0.017
	Unwashed	0.071±0.000	3.524±0.038	$0.321\pm6.00\times10^{-3}$	0.583±0.082
Plum	Washed	$0.071\pm4.00\times10^{-3}$	0.571±0.140	0.071±0.038	0.107±0.015
	Unwashed	$0.107\pm4.72\times10^{-3}$	0.975±0.034	0.125±0.010	0.250±0.020
	WHO/FAO (mg/Kg)	0.5	0.5	0.5	0.5

From the results obtained, it was shown that: -

The levels of all the metals in the unwashed fruits were high compared to the washed fruit which suggest anthropogenic sources contamination.

Chromium (Cr):

The toxic effects of Cr intake are skin rash, nasal irritation, itching and bleeding, stomach upset, kidney, liver damage, and lungs cancer. Chromium deficiency is characterized by disturbance of glucose, lipids and protein metabolism **[Khan SA, (2008)]**.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 H,2009]**. We can see from Table 4, the concentration of Chromium ranges between 0.071–0.214 mg/kg in washed fruits samples and 0.071–0.571 mg/kg in unwashed fruits samples collected from Alzawia market. The highest concentration of Chromium was determined in Unwashed Strawberries sample (0.571 mg/kg) and the lowest in Washed Apple sample (0.036 mg/kg). From the previous table, we also note that the concentration of chromium in all samples are less than the permissible limits (0.5 mg/kg) according to the World Health Organization **[OBI-IYEKE, GE(2003)]** expected Unwashed Strawberries sample.

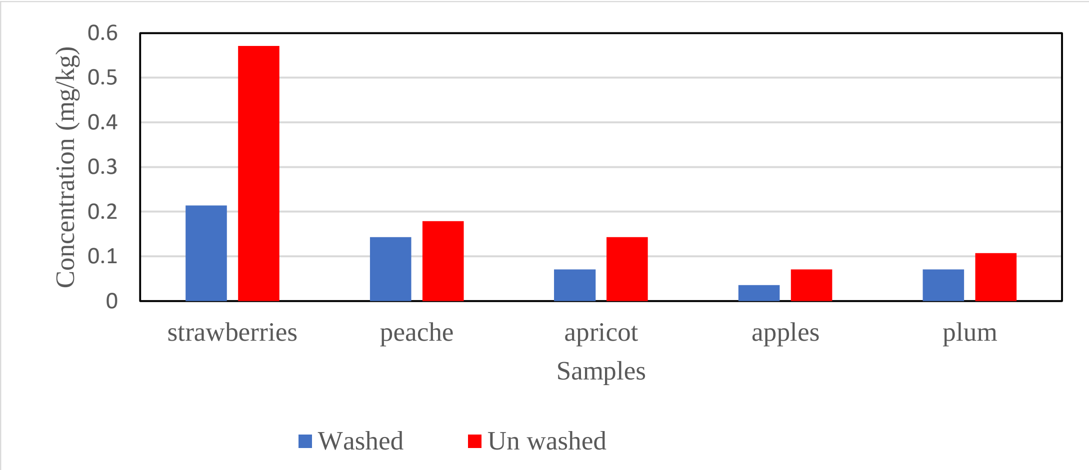


Figure 4: Concentration of Cr in fruits.

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 I,(2014)]**. We can see from Table 4, the concentration of copper ranges between 0.571–3.106 mg/kg in washed fruits samples and 0.975–3.749 in unwashed fruits samples collected from Alzawia market. The highest concentration of Cu was determined in Unwashed Peache sample (3.749 mg/kg) and the lowest in washed Plum sample (0.571mg/kg) . As can be seen from Table4. The concentration of Copper in all samples are higher than the permissible limits (0.5 mg/kg) according to the World Health Organization FAO/WHO **[OBI-IYEKE, GE(2003)]**.

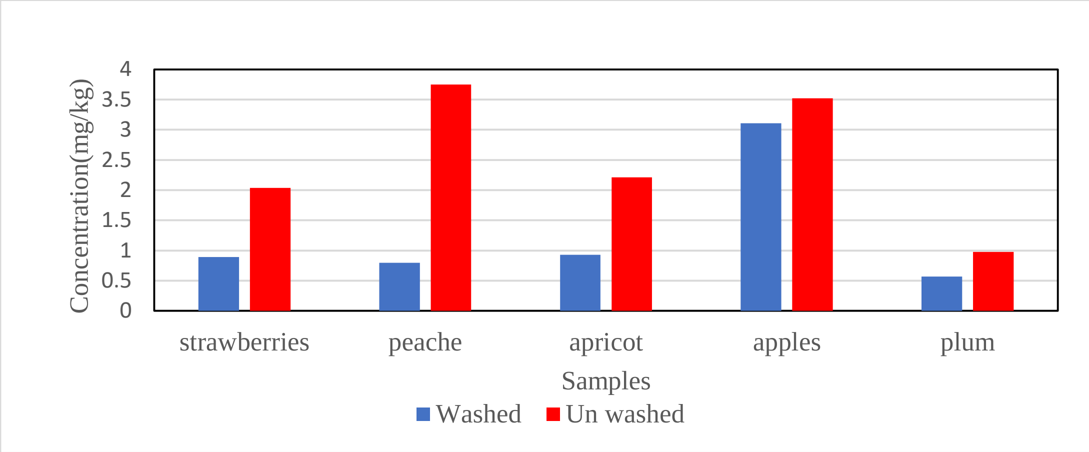


Figure 5: Concentration of Cu in fruits.

Nickel (Ni)

Nickel is required in minute quantity for body as it is mostly present in the pancreas and hence plays an important role in the production of insulin its deficiency results in the disorder of the liver **[Khan SA,2008].** We can see from Table 4, the concentration of Nickel ranges between 0.071–0.339 mg/kg in washed fruit samples and 0.125–0.678in unwashed fruit samples collected from Alzawia market. The highest concentration of Ni was determined in unwashed Peache sample (0.678 mg/kg) and the lowest in washed Plum sample (0.071mg/kg) . we also note that the concentration of Nickel in all samples are less than the permissible limits (0.5 mg/kg) according to the World Health Organization **[OBI-IYEKE, GE(2003)]** expected unwashed Peache sample.

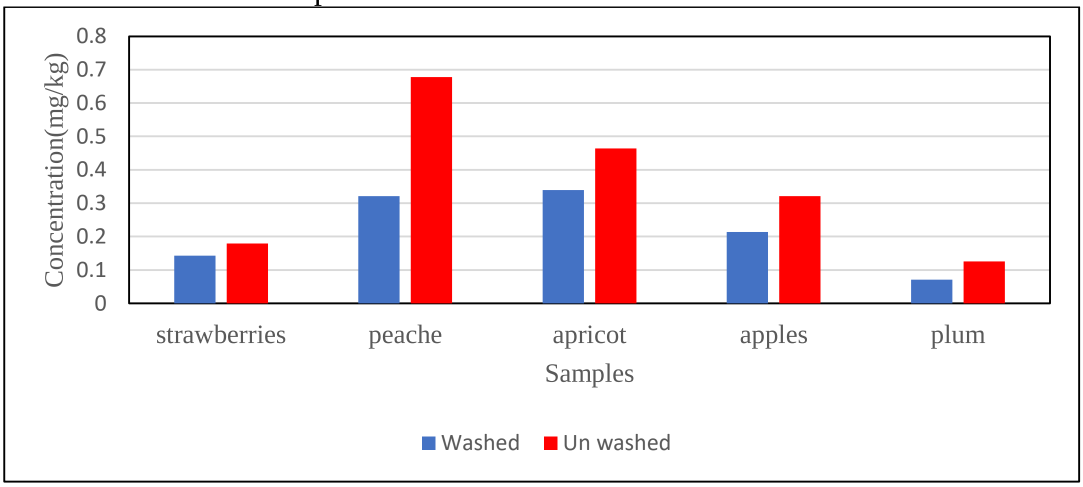


Figure6: Concentration of Ni in fruits.

Lead (Pb):

Lead is considered one of the dangerous elements to human health and causes many diseases due to its transmission from different sources and its accumulation in the human body .**[Divrikli U,2006]**. We can see from Table 4, the concentration of Lead ranges between 0.107–0.750 mg/kg in washed fruit samples and 0.250–2. 035 mg/kg in unwashed fruit samples collected from Zawia market. The highest concentration of Pb was determined in Unwashed Strawberries sample (2.035mg/kg) and the lowest in washed Plum and Apricot samples (0.107mg/kg) . As can be seen from Table4. The concentration of Lead is higher than the permissible limits (0.5 mg/kg) according to the World Health Organization FAO/WHO **[OBI-IYEKE, GE(2003)]** in unwashed Apricot, Apple, and washed and unwashed Strawberries fruit samples.

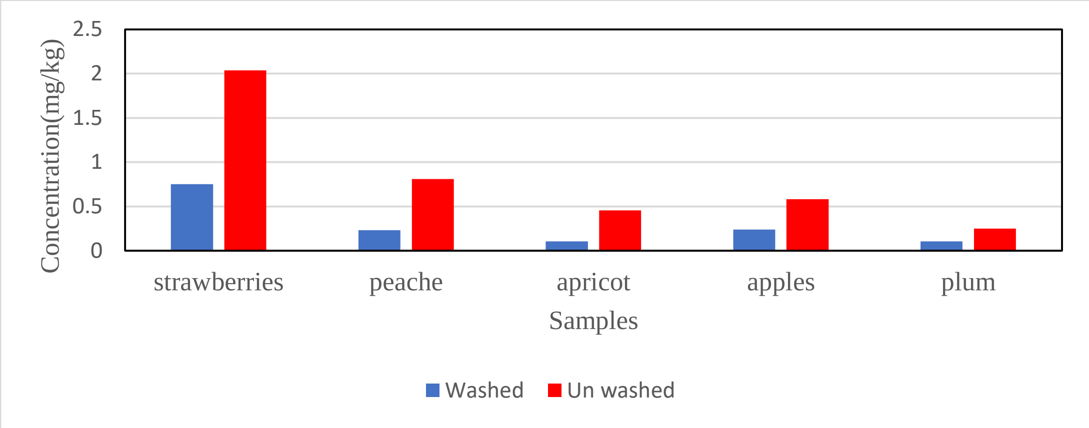


Figure7: Concentration of Pb in fruits

The average concentration of elements in all samples decreases in the following order: Cu > Pb> Ni >Cr .

4.CONCLUSIONS

Based on the analyses and results, The washing of fruits with tap water and distilled water not only remove the dirt and dust particles but also reduced the heavy metals significantly. Difference between washed and unwashed fruits with regard to heavy metal concentrations suggests that heavy metals reaches on the fruits by aerial deposition and adhere to them. Washing treatments mechanically remove the heavy metals deposited on the surface of the fruits. On the basis of present study, it is strongly recommended that fruits must be washed carefully before eating to decrease the intake of heavy metals.

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