Comparison of Locally Available Walnuts Based on Proximate Analysis and Selected Mineral Content

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Abstract

Walnut is the bullion of Pakistan. These are used as delicious nuts in cuisine. The objective of the study was proximate analysis (moisture content and ash content) and determination of toxic metals (Cadmium, lead, nickel and iron) of ten different walnut samples collected from three different locations in Lahore (Aik Moria Pull, Mall Road, Hyper Star Fortress Stadium) to determine the quality and to compare the metal profile. The heavy metals were assessed using atomic absorption spectrometer prior to wet acid digestion. The results of proximate analysis showed the ranges for moisture content 2.80– 3.29 % and ash content 1.49 – 8.64 %. The results of the trace elements detection indicated the concentrations for Cadmium 0.009 – 3.873 mg/kg, Iron 1.483 – 4.163 mg/kg, Nickel 0.980 – 2.634 mg/kg and Lead was not detected (BDL). The results revealed that all the nuts are not polluted with heavy metals as concentration of Cd, Pb, Ni and Fe are within permissible limit described by WHO. So, these nuts are safe for public consumption.

Key Words: Walnut, Heavy metals, Lahore, Proximate analysis, Atomic absorption spectrometer

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1 Introduction

Walnut is the most popular nut worldwide. These have been part of the human diet for thousands of years. These contain 65% fat, 15 % of protein and different mineral contents. Walnuts are round, single-seed nuts. Walnuts do not grow leaves till the end of spring. [1] For the protection of competing plant life these secrete chemical compounds into the earth. Due to this, flowers or vegetable now should not be grown near them. [2]

Walnuts give healthful fat, fiber, nutrients and minerals and that simply the start of how these will improve health. Walnuts are rich in antioxidant, reduce inflammation, decrease risk of some cancers, help to manage type 2 diabetes and in lowering blood pressure, support weight control, healthy aging, good brain function and male reproductive health, improves blood fats and promotes a healthy gut. Walnuts are widely available. These are present in any grocery store. These are easy to put in diet.

The elements with high atomic weight and a density at least five times greater than that of water are known as heavy metals. Arsenic (Ar), cadmium (Cd), chromium (Cr), lead (Pb), and mercury (Hg) rank among the priority of toxic metals which might be of public health importance. [3] According to the U.S. Environmental protection employer, and the international enterprise for research on cancer, these metals are also categorized as cancer agents in human beings.

0.1 ppm of earth crust is made up of cadmium. Mining, smelting and other man-made activities are the causes of cadmium dispersion in the environment through air such as phosphate fertilizer usage and sewage sludge. [4] It is typically poisonous to the kidney, particularly to the proximal tubular cells. It causes bone demineralization and increase the risk of lung cancer. [5]

Lead is the metal that has the most detrimental effects on human health. Its detrimental effects in the human beings are haemoglobin biosynthesis disruption, kidney damage, miscarriages, nervous systems disruption, brain damage and kids mastering capabilities reduction. [6]

Nickel like other heavy metals is without doubt well thought out as the most harmful and toxic metal, because it causes serious acute and chronic disorders in human beings e.g. gastrointestinal distress (such as nausea, diarrhoea, vomiting) and severe damage to kidney and lungs, pulmonary fibrosis, renal edema and skin dermatitis. [7]

Iron is likely safe for the majority while it is taken orally in suitable amounts. However, it is able to purpose harmful outcomes which include stomach dissatisfied and ache, constipation or diarrhea, nausea, and vomiting. [8]

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2   Materials and Methods

2.1   Sample Collection

Eight samples of American and Kashmiri shelled, and unshelled walnuts were picked for examination from different locations as Saleem Baba dry fruit, Aik Moria Pul and Ahmad dry fruit, Mall road Lahore in winter February 2019. Walnuts of Carrefour, and HSM Marketing were collected from Hyperstar fortress Lahore in March 2019. So, total samples were ten. Before analysis samples were given specific codes that are given in table 1.

Table 1. Specific codes of selected walnut samples

Sr. No.	Sample (Walnuts)	Location (Lahore)	Sample Codes
1	American Unshelled	Saleem Baba dry fruit Aik Moria Pul	1A
2	Kashmiri Unshelled	Saleem Baba dry fruit Aik Moria Pul	2B
3	American Unshelled	Ahmad dry fruit Mall Road	3C
4	Kashmiri Unshelled	Ahmad dry fruit Mall Road	4D
5	Carrefour Unshelled	Hyperstar Fortress	5E
6	HSM Marketing Unshelled	Hyperstar Fortress	6F
7	American Shelled	Saleem Baba dry fruit Aik Moria Pul	7G
8	Kashmiri Shelled	Saleem Baba dry fruit Aik Moria Pul	8H
9	American Shelled	Ahmad dry fruit Mall Road	9I
10	Kashmiri Shelled	Ahmad dry fruit Mall Road	10J

2.2   Sample Preparation

After the collection and labeling, Walnut samples were cleaned without washing; their shells were broken and then crushed and ground with pestle and mortar to homogenize the sample and were stored in polyethylene bags prior to further use.

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2.3 Proximate Analysis

Standard AOAC (Association of Official Analytical Chemists) methods were used for proximate analysis.

Following two analyses were done.

Moisture Content

Ash Content

2.3.1 Moisture Content

Washed crucibles were taken and dried at 90-100°C and weighed. 2 g of each walnut sample was weighed and put it in the crucible. In a hot air oven walnut samples were dried for 2 hours at 105°C. Then the crucibles were removed and cooled in desiccators to room temperature. The crucibles were weighed again and returned to oven to re-dry for 2 hours and were weighed again after cooling in the desiccators. The process was repeated until change in weight between successive drying didn't change. Each sample was analyzed in triplicate. [9] The loss of weigh was calculated as percent moisture as follow:

$$(1-2)$$

$$\% = \frac{}{1} \times 100$$

W1 = Weight of sample before drying
W2 = Weight of sample after drying

2.3.2 Ash Content

Previously oven dried walnut samples were taken and ignited to constant weight in electric muffle furnace at temperature 525-550°C. All the walnut samples were ignited to white or grey ash. Then, crucibles containing white or grey ash transferred directly to desiccators, cooled to room temperature and weighed immediately. Ash was also calculated as percent ash. Triplicate analysis for each sample was done. [9]

$$\% \, h = \frac{h \quad h}{h} \times 100$$

2.4 Digestion of Samples for Metals Detection

The digestion of walnut samples was done in aqua regia (HCl and HNO3, 3:1) for heavy metal digestion. Both the acids were used as available in the laboratory without any pretreatment. 1 gram of each walnut sample was digested in HCl (9 ml) and HNO3 (3 ml). Then each sample was heated on a hot plate with gradually increasing temperature until the complete

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decomposition of sample was done and volume reduced to about 3 ml by evaporation. Then each sample was filtered, washed with DDW (double distilled water) and transferred to a 50 ml volumetric flask quantitatively. Triplicate digestion was done for each sample for statistical data handling. A blank sample was also prepared. The samples were further analyzed by AAS for the detection of selected mineral content (Ni, Fe, Pb, Cd). [10] 2.4.1 Preparation of Double Distilled Water

Double distilled water was prepared in the laboratory. Distilled water was taken from the laboratory distill plant. Few crystals of potassium permanganate ($KMnO_4$) were added and it was redistilled.

3   Results and Discussions

The measurement of water, minerals and specific inorganic components such as Fe, Pb, Cd etc. in food is known as moisture content, ash content and mineral content respectively. These all determinations are important due to nutritional labeling because the food quality depends on the mineral present in it.

3.1   Moisture Content

Table 2. Percentage moisture content of selected walnut samples

Sample Codes	Moisture Content %			Mean
	1	2	3	
1A	2.86	3.19	3.01	3.02 ± 0.17
2B	2.86	3.28	2.99	3.04 ± 0.22
3C	2.38	3.81	3.23	3.14 ± 0.72
4D	2.38	3.33	3.33	3.01 ± 0.55
5E	2.86	2.67	2.87	2.80 ± 0.11
6F	3.33	3.33	3.22	3.29 ± 0.06
7G	2.86	3.81	2.86	3.18 ± 0.55
8H	3.33	3.11	3.01	3.15 ± 0.16

9I	3.81	2.38	3.67	3.29 ± 0.79
10J	3.33	2.86	3.2	3.13 ± 0.24

In all the samples moisture content range is 2.80 – 3.29 %. This shows that all the walnut samples contain a very low amount of water in it. It is beneficial for the preservation of walnut samples because the food with less moisture can be stored for long time without any inconvenience. There is no significant difference in shelled and unshelled walnuts moisture content. Different locations, environment and packing have also no effect on the percentage moisture content of the walnut samples. Only minute differences are seen in the moisture values (Fig. 1).
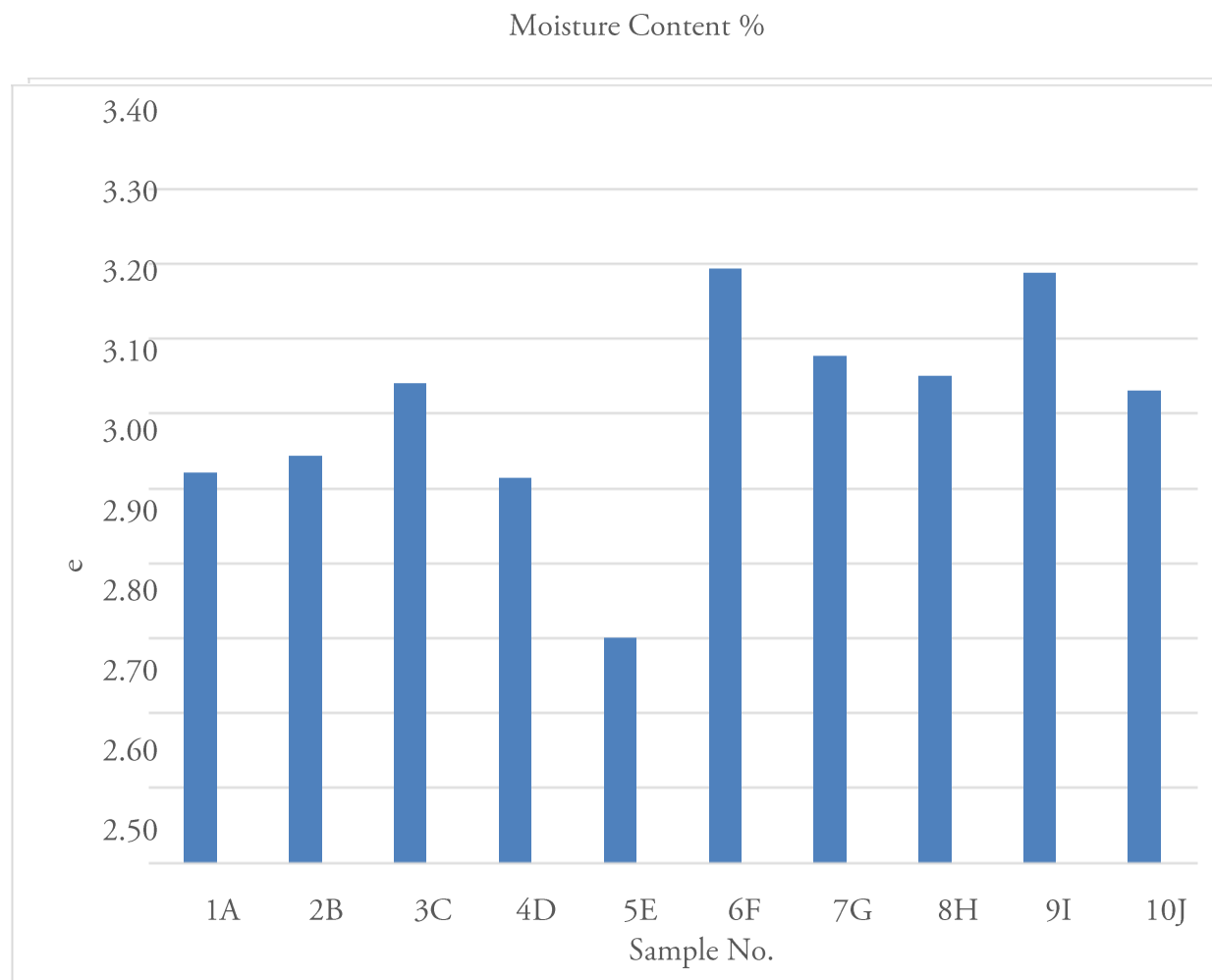
Moisture Content %

Fig. 1. Comparison of moisture content in selected walnut samples

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3.2 Ash Content

Table 3. Percentage ash content of selected walnut samples

Sample Codes	Ash Content %			Mean
	1	2	3	
1A	6.37	5.79	6.24	6.13 ± 0.30
2B	3.43	3.28	2.99	3.23 ± 0.22
3C	5.36	4.85	5.02	5.08 ± 0.26
4D	1.95	2.45	2.68	2.36 ± 0.37
5E	3.92	3.89	2.87	3.56 ± 0.60
6F	1.97	2.13	1.99	2.03 ± 0.09
7G	8.33	9.31	8.28	8.64 ± 0.58
8H	1.47	1.49	1.51	1.49 ± 0.02
9I	1.48	1.67	1.51	1.55 ± 0.10
10J	1.97	2.94	2.03	2.31 ± 0.54

Sample 7G (American shelled collected from Saleem baba dry fruit Aik Moria pull Lahore) has the highest ash content 8.64 %. It means it has the large amount of minerals and organic matter as compare to other samples. While the sample 9I (American shelled collected from Ahmed dry fruit mall road Lahore) has the low value of ash content 1.55 % among all the selected samples. The type of both walnuts is same, and both are covered with shell, but the location is different. So, the percentage ash content data show the quality difference of both shops. All the American walnuts (shelled or unshelled) have high organic matter so, have the high percentage ash content except the sample 9I. However, All the Kashmiri walnuts (shelled or unshelled), Carrefour

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CoN walnut and HSM marketing have low ash content percentage in the range 1.49 – 3.56 % (Fig. 2).
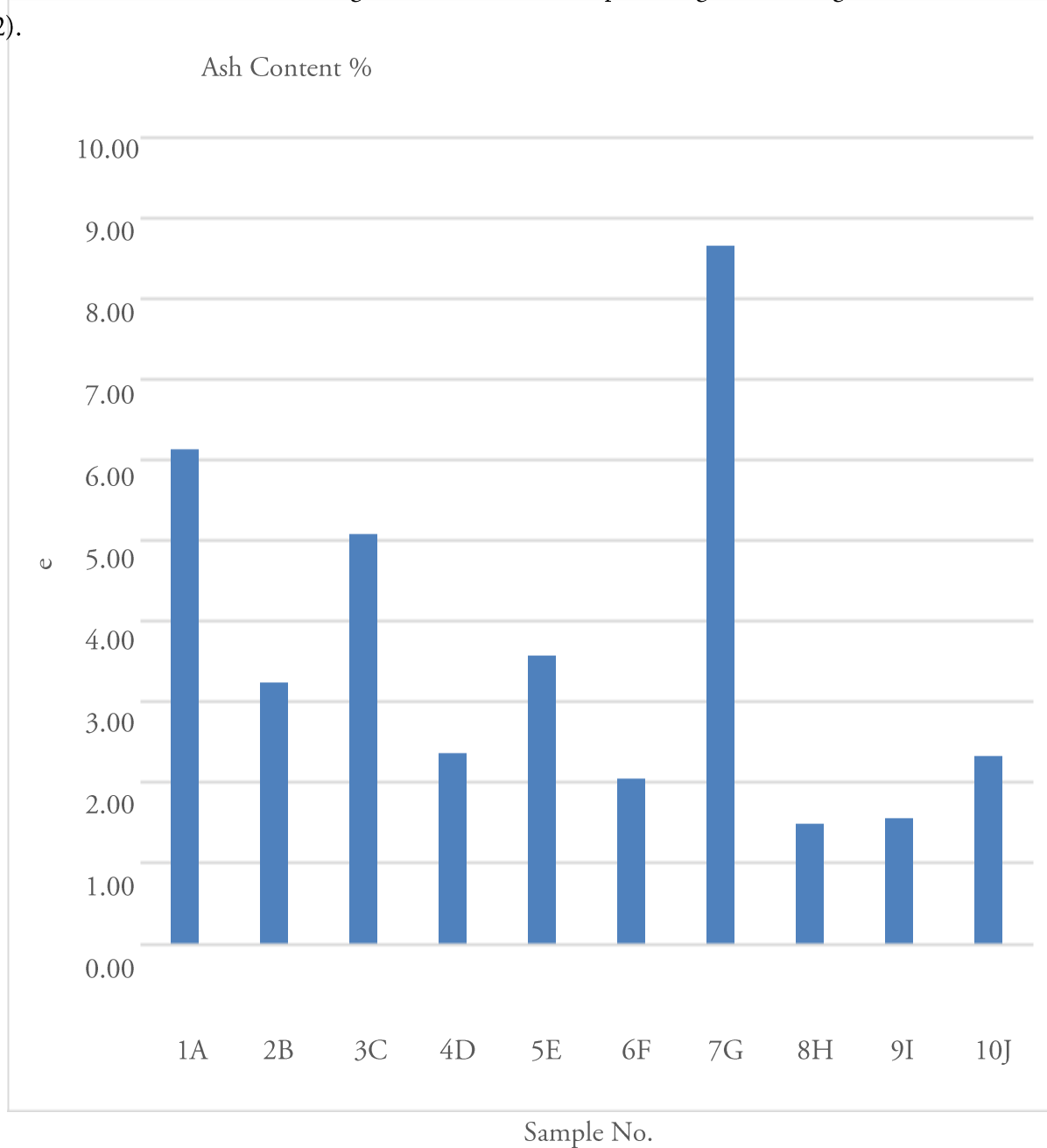

Fig. 2. Comparison of Ash content in selected walnut samples

3.3   Concentration of Cadmium

Cadmium is a hazardous metal for human health. The concentration of cadmium in all the walnut samples is given in table 4.

Table 4. Concentration of Cd in selected walnut samples

Sample Codes	Concentration of Cd (mg/kg)			Mean (mg/kg)
	1	2	3	
1A	0.169	0.159	0.15	0.159 ± 0.010
2B	0.15	0.141	0.129	0.140 ± 0.011
3C	0.099	0.121	0.101	0.107 ± 0.012
4D	0.99	1.001	1.1	1.030 ± 0.061
5E	2.16	2.17	2.01	2.113 ± 0.090
6F	3.82	3.91	3.89	3.873 ± 0.047
7G	0.006	0.008	0.012	0.009 ± 0.003
8H	1.13	1.111	1.21	1.150 ± 0.053
9I	3.32	3.126	3.145	3.197 ± 0.107
10J	2.86	2.99	2.98	2.943 ± 0.072

The range of cadmium concentration in selected walnut samples is 0.009 – 3.873 mg/kg. The cadmium concentration is within limits in all samples as stated by WHO. So, all the walnut samples are safe for human. The comparison shows that the American shelled walnuts sold at Saleem baba dry fruit Aik Moria Pull is better as compare to others because it is less polluted. Sample 1A (American unshelled picked from Saleem baba dry fruit Aik Moria Pull) has cadmium concentration 0.159 mg/kg. Both the samples are of same type but the slight difference in cadmium concentration is due to shell. All other samples also have the cadmium concentration within permissible range (Fig. 3).
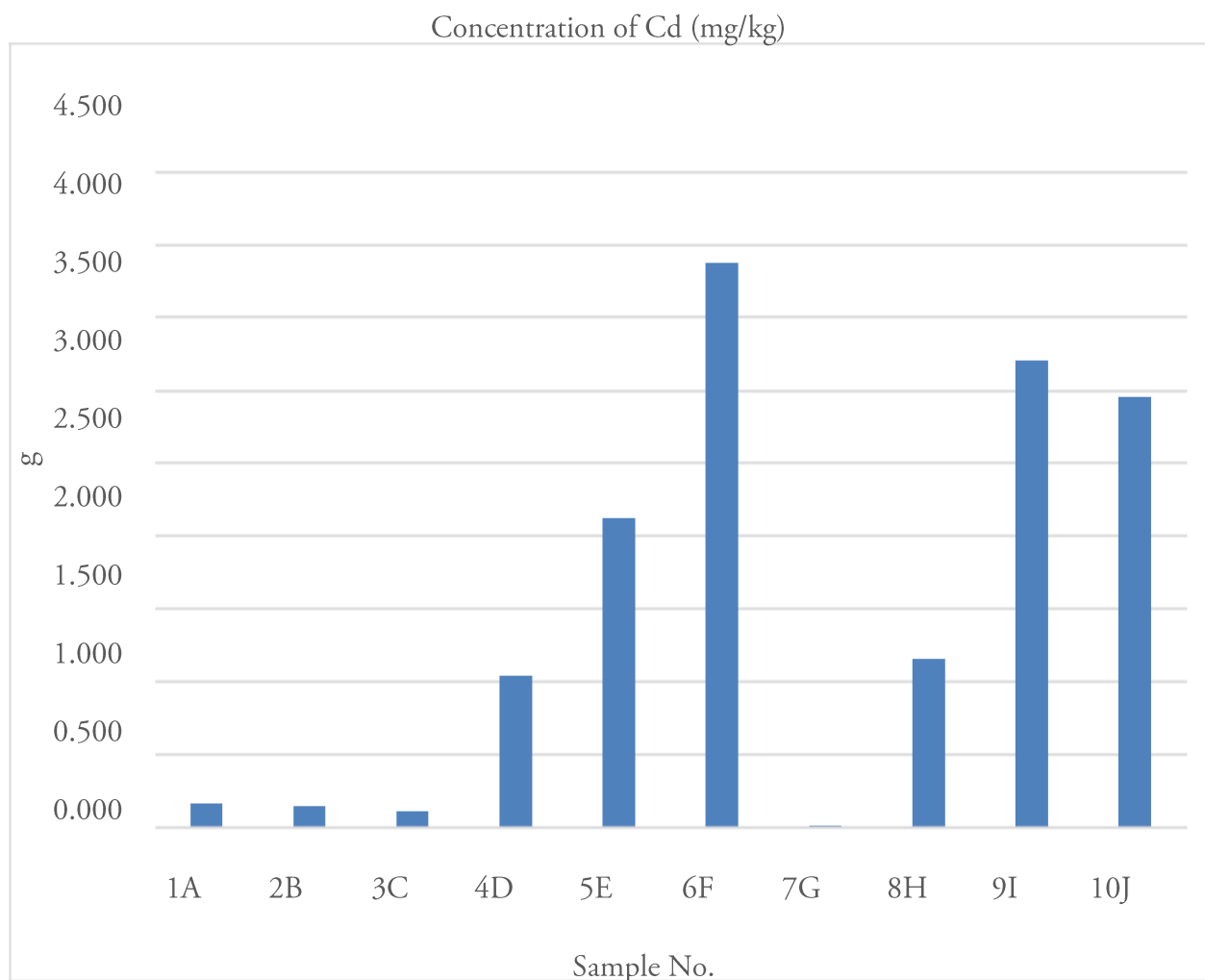

Fig. 3. Comparison of Cd concentration in selected walnut samples.

4 Concentration of Iron

Table 5. Concentration of Fe in selected walnut samples

Sample Codes	Concentration of Fe (mg/kg)			Mean (mg/kg)
	1	2	3	
1A	2.15	1.99	0.97	1.703 ± 0.640
2B	1.89	1.76	0.8	1.483 ± 0.595
3C	2.69	1.96	1.88	2.177 ± 0.446
4D	3.66	3.71	3.45	3.607 ± 0.138
5E	1.99	2.18	1.98	2.050 ± 0.113
6F	3.98	4.5	4.01	4.163 ± 0.292
7G	2.99	3.109	2.89	2.996 ± 0.110
8H	2.02	2.15	1.96	2.043 ± 0.097
9I	2.98	3.19	3.16	3.110 ± 0.114
10J	1.97	1.99	2.03	1.997 ± 0.031

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The range of iron concentration is 1.483 – 4.163 mg/kg. The iron concentration of all the walnut samples is high as compare to cadmium concentration (table 5). Iron is not harmful for human health within the limit. High quantity of iron can be dangerous. The iron concentration in all the samples is within permissible range (Fig. 4). And walnut can be used as iron supplements for those who suffer iron deficiency.
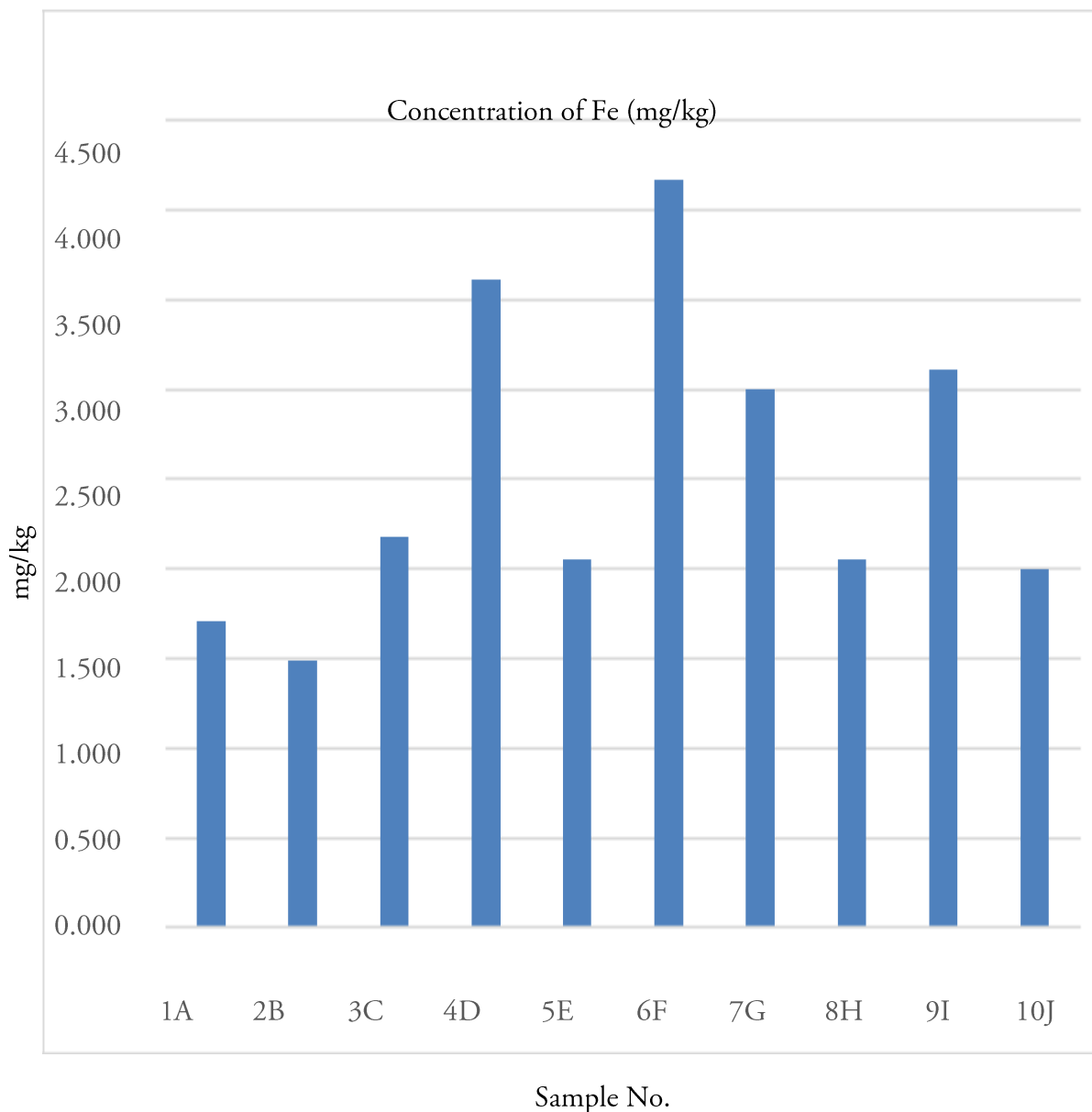

Fig. 4. Comparison of Fe concentration in selected walnut samples

3.5 Concentration of Nickel

Table 6. Concentration of Ni in selected walnut samples

Sample Codes	Concentration of Ni (mg/kg)			Mean (mg/kg)
	1	2	3	
1A	2.15	1.99	0.97	1.703 ± 0.640
2B	1.89	1.76	1.86	1.873 ± 0.068
3C	1.93	1.96	1.88	1.923 ± 0.040
4D	1.98	1.95	1.91	1.947 ± 0.035
5E	1.99	1.895	1.98	1.955 ± 0.052
6F	2.52	2.712	2.67	2.634 ± 0.101
7G	1.99	2.009	1.89	1.963 ± 0.064
8H	1.892	1.902	1.96	1.918 ± 0.037
9I	1.998	2.125	2.001	2.041 ± 0.072
10J	1.05	0.91	0.98	0.980 ± 0.070

The concentration of nickel ranges 0.980 – 2.634 mg/kg. Nickel is a harmful metal for human health, but the graph (Fig. 5) shows that all the selected walnut samples have very minute nickel concentration and these concentrations are within the WHO permissible limit. So, these samples have no harmful effect on human beings.
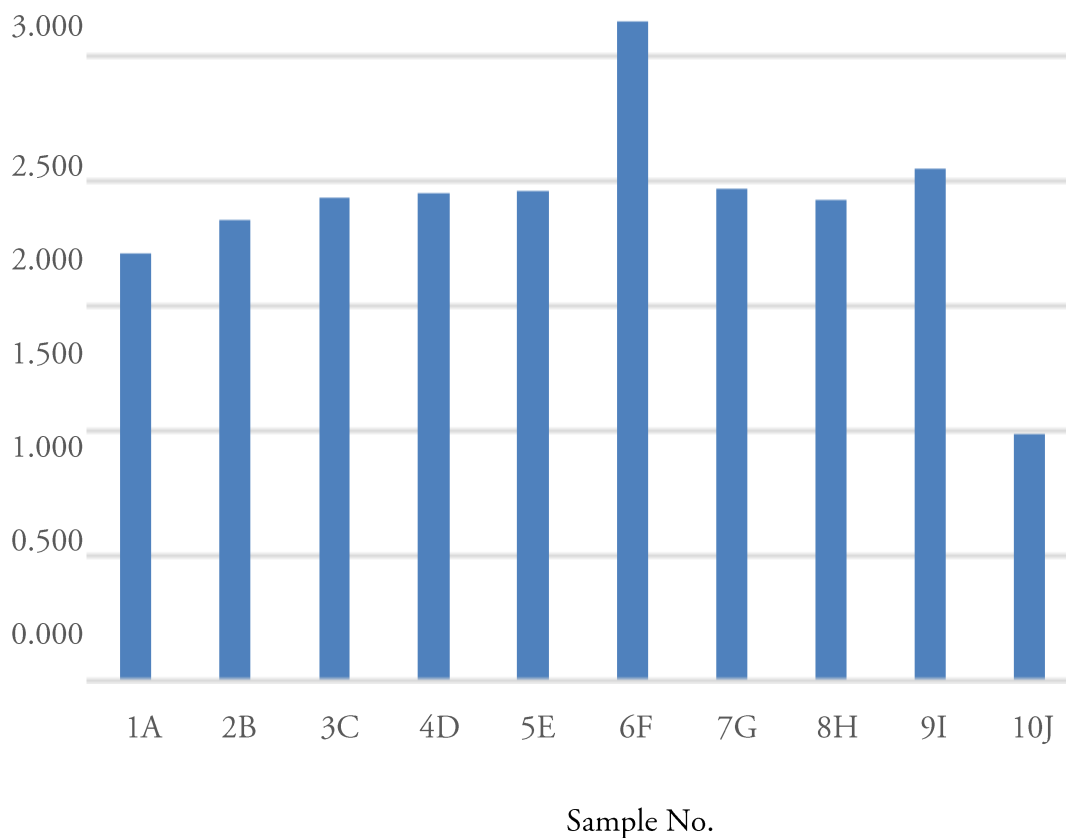
Sample No.

Fig. 5. Comparison of Ni concentration in selected walnut samples

3.6 Concentration of Lead

Table 7. Concentration of Pb in the selected walnut samples

Sample Codes	Concentration of Pb (mg/kg)		
	1	2	3
1A	BDL	BDL	BDL
2B	BDL	BDL	BDL
3C	BDL	BDL	BDL

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4D	BDL	BDL	BDL
5E	BDL	BDL	BDL
6F	BDL	BDL	BDL
7G	BDL	BDL	BDL
8H	BDL	BDL	BDL
9I	BDL	BDL	BDL
10J	BDL	BDL	BDL

The concentration of lead in all the samples is below the detection limit. This shows that all the samples are lead free. The walnuts (shelled and unshelled) from different locations of Lahore are not polluted and have no harmful effect on human health.

3.7   Comparison of Results with Literature

Table 8 shows the values of metals concentration, moisture and ash content obtained in literature of other findings. [11]

Table 8. Metals concentration, moisture and ash content values in walnut samples btained from literature

SSr. No.	Parameters	Composition
1	Fe	0.064 (mg/kg)
2	Ni	0.005 (mg/kg)
3	Pb	—
4	Cd	—

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5	Moisture %	48.70
6	Ash %	2.03

Such literature values verify the values gained through my research work. It indicates that the metals tested do not pose a health threat to customers and the walnuts are safe for public consumption without any risk of contamination from heavy metals.

But the moisture content is higher in African walnut (table 8) as compare to Pakistani walnut (table 3). Pakistani walnuts can be stored for long time due to negligible moisture content, but the African walnuts can be stored just for some time without going bad. It may be either due to environmental conditions or growing conditions. The ash content of some Pakistani walnuts match with literature value, but some samples show slight variations. It may be due to storage conditions.

4   Conclusion

Walnuts are very good source of energy. These are composed of fat, protein and different mineral contents which are beneficial for health. The metal profile shows that the quality of shelled and unshelled walnuts being sold out in the markets of Lahore is according to the consumers demand. The moisture content reveals that walnuts can be stored for long time. There are very minute variations which may be due to the storage conditions. However, these are reliable for consumption and important to take in the diet to meet up with the energy requirements of the body.

5   Future Perspectives

This research work evaluates the effects of environmental pollution in the covered and uncovered foodstuff. These results will provide an insight to the quality of locally available walnuts in different locations of Lahore. This database will help in establishing food database of walnuts as well as other dry fruits like almonds, pistachio, peanuts etc. in Pakistan as there is no database on Pakistani walnuts. There is a dire need to establish food database to assess the food quality across Pakistan. Dry fruits provide an essential part of local food industry and hence their quality during storage should be assessed on regular basis.

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