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Evaluation of Proximate, Heavy Metals and Polycyclic Aromatic Hydrocarbons Concentrations in Selected Food Stuffs in Open Markets in Port Harcourt, Nigeria

*[1]Ideriah, Tubonimi J. K., [2]Osaisai, Collins B., [3]Etukudoh, Christiana J.
[1] Institute of Pollution studies, Rivers State University, Port Harcourt.
[2]Institute of Geosciences & Space Technology, Rivers State University, Port Harcourt.
[3]Department of Chemistry, Rivers State University, Port Harcourt.
Corresponding Author: Ideriah, Tubonimi J. K.,

Abstract: *The levels of proximate components, heavy metals, Polycyclic Aromatic Hydrocarbons in some edible food stuffs obtained in Port Harcourt, Rivers State, Nigeria were assessed using standard procedures, Atomic Absorption Spectrophotometer and Gas Chromatography. The results of Proximate content ranged from 84.10% ±2.05 to 50.10% ±1.85, with utazi leaf recording the highest concentration while walnut recorded the least. Ash content value ranged from 0.62% ±0.08 to 0.15% ±0.00, carbohydrate value ranged from 18.10 % ±76.5 to 3.91% ±0.56 with the highest recorded in carrot and least in utazi leaf, lipid values ranged from 4.25% ±0.20 to 1.45% ±0.10 with the highest concentration recorded in walnut and the least in carrot, crude fibre values ranged from 20.26% ±0.10 to 0.10% ±0.01 with the highest concentration recorded in walnut and the least in green apple, protein concentration ranged from 15.75% ±0.00 to 0.87% ±0.02 with the highest concentration recorded in walnut and the least in green apple. The highest level of nickel (5.164mg/kg ±0.010) was recorded in utazi leaf while the least (1.400mg/kg ±0.010) was recorded in red apple, the highest level of chromium (11.224mg/kg ±0.010) was recorded in utazi leaf while the least (0.496mg/kg ±0.001) was recorded in red apple, the highest level of cupper (13.180mg/kg ±0.031) was recorded in walnut while the least (2.404mg/kg ±0.011) was recorded in utazi leaf, the highest level of cadmium (0.712mg/kg ± 0.011) was recorded in utazi leaf while the least (0.252mg/kg±0.005) was recorded in green apple, the highest level of lead (5.920 mg/kg ±0.010) was recorded in utazi leaf while the least level (1.076 mg/kg ±0.000) was recorded in red apple, the highest value of manganese (6.608 mg/kg ±0.005) was recorded in red apple while the least level (1.962 mg/kg ±0.001) was recorded in walnut. The concentrations of PAHs were highest in carrot (naphthalene 2.175×10^{-6} ±0.002, 2 methyl naphthalene 3.156×10^{-4} ±0.001, acenaphthylene 4.662×10^{-5} ±0.001, acenaphthene 4.849×10^{-5} ±0.003, flourene 4.481×10^{-6} ±0.002, phenanthrene 2.957×10^{-5} ±0.001, anthracene 1.030×10^{-6} ±0.002, flouranthene 1.811×10^{-4} ±0.003, pyrene 1.849×10^{-4} ±0.003, benz[a]anthracene 6.973×10^{-3} ±0.001, chrycene 3.164×10^{-4} ±0.003, benzo[b]flouranthene 3.809×10^{-5} ±0.002, benzo[k]fluoranthene 5.962×10^{-5} ± 0.001, benzo[a]pyrene 1.088×10^{-4} ±0.001, indeno[1,2,3-cd]pyrene 2.956×10^{-4} ±0.002, dibenz[a,h]anthracene 2.851×10^{-4} ±0.003) and least in utazi leaf (naphthalene 9.026×10^{-7} ±0.001, 2 methyl naphthalene 7.072×10^{-6} ±0.001, acenaphthylene 1.885×10^{-6} ±0.001, acenaphthene 1.504×10^{-6} ±0.001, flourene 2.875×10^{-7} ±0.001, phenanthrene 1.679×10^{-6} ±0.001, anthracene 3.014×10^{-7} ±0.001, flouranthene 6.196×10^{-5} ±0.001, pyrene 1.176×10^{-5} ±0.001, benz[a]anthracene 6.740×10^{-3} ±0.001, chrycene 1.448×10^{-5} ±0.001, benzo[b]flouranthene 9.713×10^{-6} ±0.001, benzo[k]fluoranthene 7.521×10^{-6} ± 0.001, benzo[a]pyrene 7.146×10^{-6} ±0.001, indeno[1,2,3-cd]pyrene 7.737×10^{-6} ±0.001, dibenz[a,h]anthracene 1.161×10^{-4} ±0.001). The highest occurring PAHs was ben[a]anthracene which values ranged from 6.973×10^{-3} ±0.001 (carrot) to 2.417×10^{-3} ±0.001 (walnut). The Concentrations of heavy metals in the samples were significantly higher than their permissible limits and so may pose adverse health concern. The food stuffs are only contaminated with PAHs. It was recommended that food stuffs should be evaluated regularly to avoid serious pollution of these food stuffs by heavy metals and PAHs. Also eating raw or unprocessed food stuff should be discouraged by relevant health authorities*

Keywords: *Food stuff, Utazi, Proximate, PAHs, Fruits, Nuts, Rivers State*

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I. Introduction

Humans rely majorly on plants for nutritional and medicinal purposes. Plants comprise of many parts which include fruits, vegetables and nuts which are widely recommended for their health promoting properties, because of their concentration of vitamins especially vitamin C and A, minerals especially electrolytes, and

more recently photochemicals especially antioxidants (Slavin and Lloyd, 2012). Fruits, vegetables and nuts can also be called food stuffs. Resent research shows that food stuffs contain concentrations of some compounds such as proximate content, heavy metals and PAHs.

Walnut (Tetracarpidium Conophorum) is a white creamy snack enveloped in a round black hard shell. (Udedi *et al.,* 2014). It is an essentially nutritious nut, having high antioxidant activity and significantly, more healthy Omega 3 – fats than any other common nut (Bi *et al.,* 2016, Hayes *et al* 2016).

Carrot (Daucus Carota) is a root vegetable that has crunchy taste and highly nutritious. It is a good source of Beta – Carotene, fiber, vitamin K, potassium and antioxidant. (Alklint *et al.,* 2003).

Utazi leave (Gangronema Latifolium) is a vegetable and has been shown to increase the effectiveness of reproductive hormones and help to raise low sperm count. (https://www/.Naija.ng/1122422-Utazi-leaf-fertility-what-effect.html #1122422).

Green and red apples (Malus Domestica) are fruits high in fibre, vitamin C and various antioxidants. They are also very filling, considering the low Calorie content. Study shows that eating apple has multiple benefits for health (Jeanelle and Rui 2004).

PAHs are organic substances made up of carbon and hydrogen atoms grouped into atleast two condensed or fused aromatic ring structure (CCME, 2012). They are a class of organic compounds consisting of two or more fused aromatic rings. PAHs arise from oil seepages and erosion of petroliferous states, incomplete combustion of wood and biomass via forest and grass fiber (Christopher *et. al.,* 2017).

Heavy metals are naturally occurring elements that have a high atomic weight and a density at least 5 times greater than that of water. They include Cu, Pb, Mn, Cr, As, Cd and Ni. They cannot be degraded or destroyed. although heavy metals are naturally occurring elements that are found throughout the earth's crust, their multiple industrial, domestic, agricultural, medical and technological, applications have led to their wide distribution in the environment, raising concerns over their potential effects on human health and the environment.

Proximate composition analysis of food includes Moisture, carbohydrate, ash, crude fiber, lipid and protein contents.

The aim of this study is to evaluate the levels of proximate content, PAHs and Heavy Metals in apples, walnuts, carrots and utazi leaves.

Food stuffs such as fruits, vegetables and nuts are the main source of food supplement for humans. Studies (Slavin and Lloyd, 2012; Bi *et al.,* 2016, Hayes *et al.,* 2016) have shown that fruits and vegetables which are consumed daily by humans contain some amount of heavy metals which may be toxic to health.

Since some of these food stuffs are eaten raw from the market and due to the toxicity of the PAHs and heavy metals to health it is necessary to carry out this study to evaluate these parameters in the selected food stuffs consumed in Rivers State to create awareness among the consumers.

Plate 1: Carrot (Daucus carota)
Plate 2: Utazi leaf (Gangronema latifolium)

Plate 3: Red apple and Green apple (Malus domestica)

Plate 4: Walnut (Tetracarpidium conphorum)

Plates showing selected food stuff samples

The Study Area

Oil mill market is one of the largest busy and highly populated markets in Rivers State. It holds every Wednesdays in Rumuochurlu community in Obio Akpor L.G.A. in Rivers State, Nigeria. Varieties of items such as food stuffs, clothes, foot wears, hairs accessories and many more items from within the state and neighbouring state such as Abia State and Akwa Ibom State are sold at affordable prices. Although the samples were collected from oil mill markets, same food stuffs are being sold in several other markets in Port Harcourt and its environs.

II. Materials and Method

Sampling site selection and location

The sampling site was selected based on population and widely people come from far and near to buy and sell in the market. Food stuffs samples ware purchased from oil mill market.

Each of the samples was later placed in an oven at about 105^0C for complete dryness. The dry samples were grounded into its powdery foam. Each of the samples was stored in well labeled containers for proximate analysis and heavy metals while that of PAHs were stored in a well labeled bottle container.

Samples collection and preparation

The food stuff samples such as carrot, green apple, red apple, utazi leaf and walnut were collected, sorted and cleaned. The Apples, Carrot and Walnut were cut into sizable pieces using knife. While the utazi leaf was handpicked, washed using distilled water and air dried.

The samples were weighed and homogenized. Samples for proximate content and heavy metals analysis were stored in well labeled plastic containers while samples for PAHs analysis were stored in glass sampling bottles.

Analytical methods

Atomic Absorption Spectrophotometer

The standard procedure described by AOAC (2002) was used for the analyses of heavy metals. Samples were digested using exactly 1.0g of the milled sample into a digesting glass tube. 12ml of HNO_3 was added to the food samples and mixtures were kept overnight at room temperature. Then 4.0ml perchloric acid ($HClO_4$) was added to this mixture and was kept in the fume block for digestion. The temperature was increased gradually, starting from 30^oC and increasing up to 250 ^{o}C – 300^oC. The digestion was completed in about 70 – 85mins as indicated by the appearance of whiter fumes. The mixture was left to cool down and the contents of the tubes were transferred to 100ml flask.

The atomic absorption spectrometer suggested by American society for testing and materials (ASTM, 2010) was used to determine heavy metals (Ni, Cr, Cu, Cd, Pb, Mn).

Gas Chromatography (GC)

Concentrated aromatic extract of the selected samples were transferred into labeled glass vials with Teflon or rubber crimp caps for GC analysis. 1µL of the concentrated samples was injected by means of a hypodemic syringe through a rubber septum into the column of Gas Chromatograph (HP 5890 SERIES II). Separation occurs as the vapour constituent partition between the gas and liquid phases.

Proximate Analysis

The recommended methods of the Association of official Analytical Chemists (AOAC, 1990) were used for the determination of moisture, ash, crude fibre, crude protein and carbohydrate in the different food samples.

1. Determination of moisture content

Percentage determination by Air Oven moisture content of the samples was done using standard method (AOAC, 2005). An empty clean crucible was weighed. Some grams of the wet samples was weighed into a crucible and dried in an oven at 105^0c Constant weight. The evaporating dish was cooled in desiccators to room temperature then it was re- weighed and recorded.

Calculation:

$$\% \text{ Moisture} = \frac{\text{Weight of fresh Sample} - \text{Weight of Dried Sample}}{\text{Weight of sample used.}} \times \frac{100}{1}$$

2. Determination of ash content

Sample were weight into a clean porcelain crucible which was previously preheated and weight. The crucible was inserted into a muffle furnace and regulated to a temperature of 630^0c for three hours and allowed to cool to room temperature and re-weighted.

Calculation:

$$\% \text{ Ash} = \frac{\text{Weight of crucible + Ash sample Weight of crucible}}{\text{Weight of sample}} \times \frac{100}{1}$$

Or

$$\frac{\text{Weight of Ash}}{\text{Weight of sample}} \times \frac{100}{1}$$

3. **Determination of crude fat (%)**

Same grams of the sample were weighed and inserted into a filter paper and was placed into a soxhlet extractor. The extractor was placed into a pre-weighed dried distillation flask. Then the solvent (acetone) was introduced into the distillation flask via the condenser end attached to the soxhlet extractor. The set up was held in place with a retort stand clamp. Cooled water jet was allowed to flaw into the condenser and then heated solvent chamber was extracted in the process of continuous refluxing. When the up was observably extracted completely from the sample under test, the condenser bond the extractor was disconnected and the solvent was evaporated to concentrate the lipid. The flask was then dried in the air oven to constant weight and re-weighed to obtain the weight lipid

Calculation:

$$\% \text{ Lipid} = \frac{\text{Weight of flask and extract} - \text{Weight of empty flask}}{\text{Weight of sample extracted}} \times \frac{100}{1}$$

4. Determination of crude fibre

Crude fibre was determined using Muslin cloth method

Principle: The samples were subjected to acid digestion followed by alkali digestion and the remaining residue was weighed and ashed. The loss of weight after ashing was crude fiber content of the feed.

Procedure: 2g of each sample and 200ml of 0.255N H_2SO_4 were placed in a 600ml lipless beaker and placed on an electrical heater. A suitable condensing found bottom flask was placed over the beaker. The heater was switched on. The purpose of keeping a condensing flask filled with cold water was for condensing back the evaporating acid to the beaker. This maintains the volume of the acid without reduction.

Digestion in acid: The beaker was heated to bring acid (0.255N H_2SO_4) to boiling stage. Then 2g of the substance was transferred to the boiling. The acid boils and the feed was digested in acid. This boiling and digestion were continued for 30mins. After the 30mins the boiling was stopped and the condenser removed.

Filtration: A funnel was place in a large conical flask and the cloth fixed over the funnel. The content from the beaker was transferred to the filtering funnel. After all the acid and acid digested residues are transferred to the linen cloth, the beaker was washed with distilled water and transferred to the filtering funnel. The washed was contained till the residue was made acid free.

Test: This was tested by placing one two drops of the filtrate on a blue litmus paper. The blue litmus paper remained blue implying that the residue was washed free from acid. After complete washing the filter cloth was taken along with the residue and squeezes to remove the water from the residue. The cloth was placed over porcelain slab. The adhering residue was scrapped gently from the filter cloth and kept in the center of the filter cloth.

Digestion in Alkali: The acid digested residue was than subjected to alkali digestion. The 200ml of sodium hydroxide (0.313N) was poured into a lipless beaker (600ml capacity), placed over the heater and a condensing

flask fixed over it. The alkali solution was boiled by heating. When it started boiling the condensing flask was removed and the acid digested residue transferred to the boiling alkali. The condensing flask was replaced act heating continued. The residue was digested in the boiling NaOH for about 30minutes. After 30mins, the condenser was removed and content transferred to a filtering funnel. The residue was washed repeatedly with distilled water till it was alkali free.

This was tested by placing one or two drops of the filtrate on a red litmus paper. It remained red indicating that residue was free of alkali. When the residue was free from alkali the cloth squeezed to dry the residue. The residue was transferred without any loss to a clean silica crucible.

Note: The cold water in the condensing flask should never be hot.

Drying and Weighing: The crucible was placed in preheated hot air oven (110^0C) over night. This was to drive off the moisture completely. After complete drying, the crucible was cooled in desiccators. It was weighed along with the residue. The crucible heated with electrical Bunsen burner in order to ash the residue. The heating was continued till a whitish ash appeared. The crucible was cooled to room temperature and weighed.

5. Determination of protein

Analysis for protein determination was done in different stages:

Digestion [stage 1]

0.1g of each samples were weighed into a clean conical flask of 250ml capacity, 3g of digestion catalyst was added into the flask and 20mls cone Sulphuric acid was also added and the sample were shaken was heated to digest.

The colours of the samples changed from black to sky blue coloration. The digested samples were cooled to room temperature and were diluted to 100ml with distilled water.

Distillation (stage 2)

Distillation procedure was then performed on the digested) samples using digestion and 20ml of diluted digest was measured into a distilled flask and the flask was held in place on the electron thermal heater or hot plate. The distillation flask was attached and a Liebig condenser connected to a receiver containing 10mls of 2% bone and indicator. 40mls sodium hydroxide was injected into the digest via a syringe attached to the mono-arm steelhead until the digest became strongly alkaline. The mixture was heated to boiling and the distilled ammonia gas via the condenser into the receiver beaker. The colour of the bone change from purple to greenish as ammonia distillate was introduce into the boric acid.

Titration (Stage 3)

The distillate was titrated with standard 0.1N hydrochloride acid soil back to purple from greenish. The volume of hydrochloride acid added to effect this change was recorded as titer value.

Calculation:

$$\% \text{ organic nitrogen} = \frac{\text{titre value} \times 1.4 \times 100 \times 100}{1000 \times 20 \times 0.1}$$

Where titer value = the volume of HCl used in titrating the NH3 distilled 1.4 = Nitrogen equivalent to the normality of HCl used in the titration 0.1N.

100 = the total volume of digest dilution
100 = Percentage factor
1000 = Conversion factor from gram to milligram
20 = Integral volume of digits analyses or distilled
0.1 = the weight of sample gram digested.

6. Determination of Carbohydrate

0.1g of each samples were weight into a 25mls volume the flask. 1ml of distilled water and 1.3mls of 62% perchloric acid was added and shaked for about 20mins to homogenize completer. The flask was made up to 25mls mark with distilled water and stopper. The solution formed was filtered through a gas filter paper or allowed to sediment into a 10ml test tube. This was dilute into volume with distilled water, 1ml of working solution was pipette into a clean test tube and 5mls anthrone reagent was mixed. Similarly and the whole mixture were read at 630nm wave length using the 1ml distilled water and the 5ml anthrone reagent prepared and was treated as sample with anthrone reagent. Absorbance of the standard glucose was read and this value of carbohydrate as glucose was calculated using the formula below.

Calculation:

$$\% \text{ CHO as glucose} = \frac{25 \times \text{absorbance of sample}}{\text{absordance of Standard glucose} \times 1}$$

III. Results and Discussions

Results

The result of proximate composition, heavy metals and Polycyclic Aromatic Hydrocarbons in selected food stuffs while Fig. 4.1-4.2 show comparison between green and red apple and Fig 4.3 show result of PAHs.

Table 1. Mean Levels of Proximate Content measured in selected food samples

S/N	Sample Identity	Moisture (%)	Carbohydrate (%)	Ash (%)	Lipid (%)	Crude fibre (%)	Protein (%)
1	Utazi	84.10 ±2.05	3.91 ±0.56	0.15 ±0.00	1.59 ±0.25	5.00 ±0.18	5.25 ±0.02
2	Red Apple	74.10 ±2.02	19.21 ±0.82	0.20 ±0.01	3.27 ±1.02	0.99 ±0.10	1.31 ±0.01
3	Green Apple	78.88 ±2.04	16.21 ±0.81	0.42 ±0.06	3.31 ±1.02	0.10 ±0.01	0.87 ±0.02
4	Walnut	50.10 ±1.85	9.54 ±0.68	0.30 ±0.05	4.25 ±0.20	20.26 ±0.10	15.75 ±0.00
5	Carrot	75.76 ±2.03	18.10 ±0.76	0.62 ±0.08	1.45 ±0.10	0.53 ±0.10	3.50 ±0.20

Proximate Composition

Moisture content ranged from 84.10% ±2.05 to 50.10% ±1.85, the highest level was recorded in utazi leaf and the least in walnut. The concentration trend was not consistent, it followed the pattern utazi > Green apple > Carrot > Red apple >walnut.

Ash content of the selected sample ranged from 0.62% ±0.08 to 0.15% ±0.00 with the highest level recorded in carrot and the least in utazi. Concentration trend was not consistent, it followed the pattern, Carrot > Green apple > Walnut > Red apple > Utazi leaf.

Carbohydrate levels ranged of the selected samples ranged from 19.21% ±0.82 to 3.91% ±0.56. The highest value was recorded in red apple and the least in utazi leaf. The concentration followed the trend, Red apple > Carrot > Green apple > walnut > utazi leaf.

Crude fibre content of the selected samples ranged from 20.26% ±0.10 to 0.10% ±0.01 with the highest level recorded in walnut and least in green apple. Concentration levels followed the trend, Walnut > Utazi > Red apple > Carrot > Green apple.

Lipid levels ranged from 4.25% ±020 to 1.45% ±0.10 with the highest value recorded in walnut and the least in carrot. The concentration followed the trend, Nut > Fruits > Vegetables.

Crude protein values range from 15.75% to 0.87% with Walnut giving the highest value whereas green apple gave the least protein content.

In this study, crude fibre in walnut was relatively high (20.22%) compared to other food stuff samples which ranged from 5.00% to 0.10%

Carbohydrate content ranged from 19.27% to 3.19% with the highest value recorded in Red apple (19.27%) and lowest in Utazi (3.91%).

Table 2. Mean Levels of Heavy Metals Measured In Selected Food Stuffs

S/N	Samples Identification	PAH (mg/kg)	Ni (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Mn (mg/kg)
1	Green Apple	<0.001	1.932±0.0	0.840±0.01	3.428±0.00	0.252±0.05	1.416 ±0.00	6.608±0.05
2	Red Apple	<0.001	1.400±0.0	0.496±0.01	2.500±0.01	0.272±0.02	1.076±0.00	3.108±0.05
3	Utazi leaf	0.007	5.164±0.01	11.224±0.01	2.404±0.01	0.712±0.01	5.920±0.01	5.568±0.10
4	Walnut	0.003	4.028±0.01	2.804±0.01	13.18±0.01	0.296±0.01	3.364±0.01	1.962±0.01
5	Carrot	0.009	3.872±0.02	7.996±0.05	10.82±0.01	0.372±0.01	4.312±0.01	3.876±0.01
Safe limit (WHO & FAO, 2012)			0.20	0.10	0.20	0.20	0.30	0.20

Heavy Metals

High Nickel level was recorded in Utazi leaf (5.164 mg/kg) while the least was recorded in red apple. The level in Green and Red Apple (fruits) were significantly low compared to that of vegetables and nut.

The highest Cr level (11.224 mg/kg) was recorded in Utazi leave was recorded in Red while the least was recorded in red apple. The study revealed that the trend of chromium levels followed fruits < nuts < vegetables.

The range of cupper was between 13.184mg/kg and 2.404 mg/kg with the lowest concentration recorded in utazi leaf (2.404mg/kg) and the highest in walnut (13.184mg/kg).

The lowest Cadmium was recorded in while the highest was recorded for Utazi leave (0.712 mg/kg). The result shows that the samples had relative low Cd lowest in fruits and nut.

Lead (Pd): lead range was between 1.076 mg/kg to 5.920 mg/kg. The lowest lead was recorded in Red Apple while the highest was recorded in Utazi leaf. The result showed that the concentration of lead is lower in fruits compared to nut and vegetables.

Manganese (Mn): The lowest level of Mn was recorded in walnut (1.962 mg/kg) and the highest was recorded in green apple. The result shows that green apple contained significantly higher amount of Mn than Red Apple. Its concentration in Green Apples was twice that of red apple leaves also contain a significant amount of Mn.

Green Apple: from the results, green apple was observed to contain higher levels of heavy metals than red apple.

All the food stuff samples were contaminated with heavy metals but utazi leaf had the highest concentrations. Concentrations of heavy metals exceeded the permissible limit by WHO/FAO 2012.

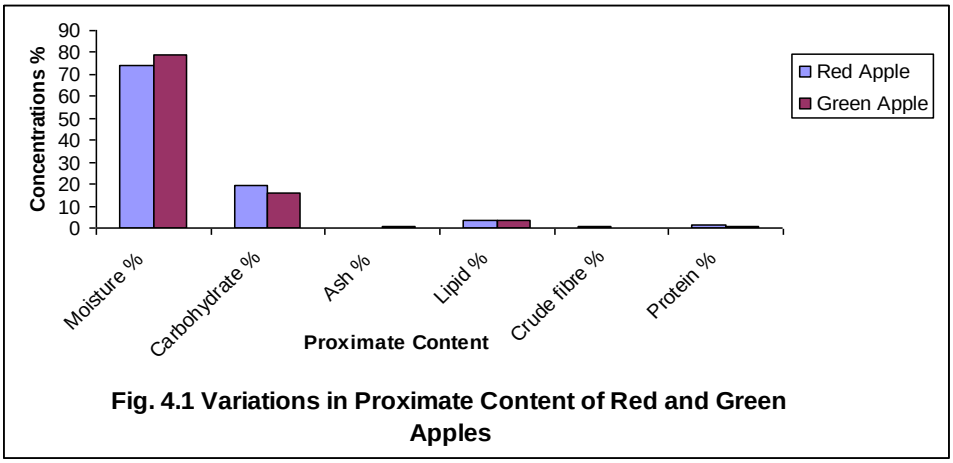

Fig. 4.1 Variations in Proximate Content of Red and Green Apples

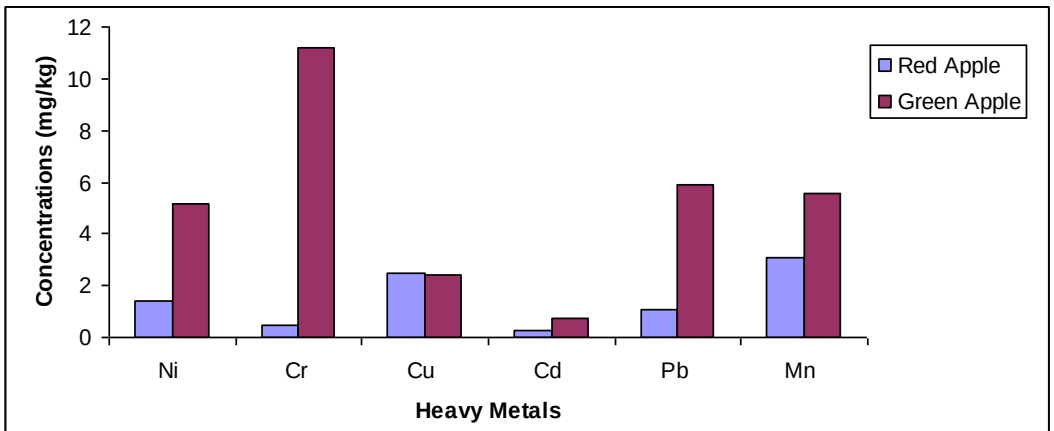

Fig. 4.2 Variations in Heavy Metal Concentrations in Red and Green Apples

Table 3. Levels of Polycyclic Aromatic Hydrocarbons Measured In Selected Food Stuffs

S/N	PAHs	Green Apple	Red Apple	Utazi leaf	Walnut	Carrot
1	Naphthalene	< 0:5	< 0.05	$9.026 \times 10^{-1} \pm 0.001$	$9.553 \times 10^{-7} \pm 0.001$	$2.175 \times 10^{-6} \pm 0.002$
2	2 methyl Napthalene	”	“	$7.072 \times 10^{-6} \pm 0.001$	$1.014 \times 10^{-5} \pm 0.001$	$3.156 \times 10^{-4} \pm 0.001$
3	Acenaphylene	”	“	$1.885 \times 10^{-6} \pm 0.001$	$2.790 \times 10^{-6} \pm 0.001$	$4.662 \times 10^{-5} \pm 0.001$
4	Acenaphthene	”	“	$1.504 \times 10^{-6} \pm 0.001$	$2.781 \times 10^{-6} \pm 0.001$	$4.849 \times 10^{-5} \pm 0.003$
5	Flourene	”	“	$2.875 \times 10^{-7} \pm 0.001$	$5.048 \times 10^{-6} \pm 0.001$	$4.481 \times 10^{-6} \pm 0.002$
6	Phenanthrene	”	“	$1.679 \times 10^{-6} \pm 0.001$	$3.745 \times 10^{-6} \pm 0.001$	$2.957 \times 10^{-5} \pm 0.001$
7	Anthracene	”	“	$3.014 \times 10^{-7} \pm 0.001$	$1.007 \times 10^{-6} \pm 0.001$	$1.030 \times 10^{-5} \pm 0.002$

8	Flouranthene	”	“	$6.196 \times 10^{-5} \pm 0.001$	$4.551 \times 10^{-5} \pm 0.001$	$1.811 \times 10^{-4} \pm 0.003$
9	Pyrene	”	“	$1.176 \times 10^{-5} \pm 0.001$	$3.288 \times 10^{-5} \pm 0.001$	$1.849 \times 10^{-4} \pm 0.003$
10	Benz[a]anthrane	”	“	$6.740 \times 10^{-3} \pm 0.001$	$2.417 \times 10^{-3} \pm 0.001$	$6.973 \times 10^{-3} \pm 0.001$
11	Chrysene	”	“	$1.448 \times 10^{-5} \pm 0.001$	$1.084 \times 10^{-5} \pm 0.001$	$3.164 \times 10^{4} \pm 0.003$
12	Benzo[b]fluoranthene	“	“	$9.713 \times 10^{-6} \pm 0.001$	$1.013 \times 10^{-5} \pm 0.001$	$3.809 \times 10^{-5} \pm 0.002$
13	Benzo[k]fluoranthene	“	“	$7.521 \times 10^{-6} \pm 0.001$	$2.063 \times 10^{-5} \pm 0.001$	$5.962 \times 10^{-5} \pm 0.001$
14	Benzo[a]pyrene	“	“	$7.146 \times 10^{-6} \pm 0.001$	$8.714 \times 10^{-6} \pm 0.001$	$1.088 \times 10^{-4} \pm 0.001$
15	Indeno[1,2,3-cd]pyrene	“	“	$7.737 \times 10^{-6} \pm 0.001$	$8.606 \times 10^{-6} \pm 0.001$	$2.954 \times 10^{-4} \pm 0.002$
16	Dibenz[a,h]anthracene	“	“	$1.161 \times 10^{-4} \pm 0.001$	$4.536 \times 10^{-6} \pm 0.001$	$2.851 \times 10^{-4} \pm 0.003$
ND= Not Detected; Permissible limit 0.01mg/kg – 0.001mg/kg by WHO and SON						

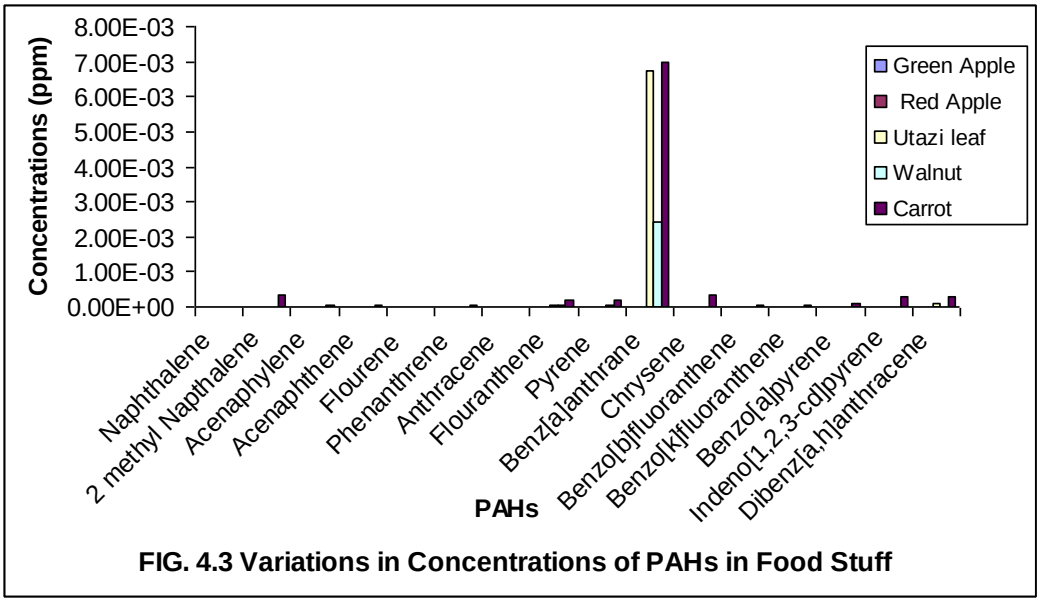

FIG. 4.3 Variations in Concentrations of PAHs in Food Stuff

PAHs

The study shows that the highest concentration of Naphthalene was recorded in carrot and the least was recorded in utazi leaf. The Naphthalene concentration was below permissible limit of 0.04mg. 2-Methyl Naphthalene highest Concentration was recorded in carrot and the least in utazi leaf. Acenaphthylene highest concentration was recorded in carrot and the least in utazi leaf. The highest concentration of Fluorene was recorded in walnut and the least in utazi leaf. Phenanthrene highest level was recorded in carrot and the least in walnut. Anthracene highest concentration was recorded in carrot and the least in walnut. Flouranthene highest concentration was recorded in carrot and the least in walnut. Pyrene highest concentration was recorded in carrot and the least in utazi leaf. Benz[a]anthracene highest concentration was recorded in carrot and the least in walnut. Chrysene highest concentration was recorded in carrot and the least in walnut. Benzo[b]fluoranthene highest level was recorded in carrot while the least was recorded in utazi leaf. Benzo[k]fluoranthenen highest level was recorded in carrot while the least recorded in utazi leave sample. Benzo[a]pyrene highest level was recorded in carrot while the least was recorded in utazi leave. Indeno[1,2,3-cd]pyrene highest level was recorded in carrot while the least was recorded in utazi leave. Dibenz[a,h]anthracene highest level was recorded in carrot, while the least was recorded in walnut. The results of each sample shows that green and red apple had no significant concentration of PAHs while, Carrot had highest concentration of some PAHs except Benz (a) anthracene.

IV. Discussions

1. Proximate composition

A close observation of the result reveals that all the selected samples had appreciable levels of nutrients must especially moisture. Utazi leaf was recorded to have the concentration of moisture, this must have been has as a result of large surface area of the leaf which are wide spread with stomata of about 1000 to 100,000 (Krogh,

2010) distributed on the leaf surface. In most cases, sellers of utazi leaf constantly sprinkle water on the leaf while in the market to prevent it from drying, and the water due to the large surface area of the leaf and large stomata are easily trapped into the leaf, thus, increasing the level of moisture in the leaf. The samples were collected in rainy season and this may also be the reason for high levels of moisture observed in the selected samples. The high level of moisture in vegetables in this study agrees with that of Emmanuel *et al.,* (2013).

Fruits were also observed to have high concentration of moisture (not higher than vegetables). This may be because lesser quantity of water is strapped from the environment because of the structures of the selected food stuffs (round with small surface area). Water content present in it are being distributed to it by leaves of the plants and also while in market, theses fruits are cleaned dry form water to avoid quick spoilage and also these apples are imported from outside Nigeria, this may also affect the moisture or nutrients levels of the fruits due to the fact that it takes weeks if not months for these fruits to get to Nigeria and during that period of importing, nutritional content most have reduced and the fruits wont b e as fresh as when plucked from the plant.

Nut was observed to have least concentration of moisture and higher concentration of lipid, crude fiber and protein. This may be as a result of the nature of the nut, (nuts are covered with hard outer shell and jelly-like inner shell before the flesh. Water that is distributed to it or settles on it is first absorbed by the hard outer shell and the little that passes through the hard shell and also absorbed by the inner shell and just little or minute quantity will get to the flesh. The concentration of moisture of moisture in nuts affects the concentration of other nutrients. The study revealed that Walnut is a very good source of protein significant difference was observed in crude protein of each food/stuffs.

Relatively low crude protein in fruits (Green and Red Apple) agrees with Fila *et al.,* (2013), that fruits are low in total nitrogenous components compared to seeds, leaves and some other plant parts and tissues.
Due to the fact that the selected food stuffs were rich in nutrient, they can be good recommendation for health issues since it can aid indigestion (crude fiber and moisture), constipation, lower cardiovascular disease risk, obesity, reduce calories absoption, and improve gut health (Slavin *et al.,* 2012).

2. Heavy metals

All the selected food stuffs were contaminated with the analyzed heavy metals. This contamination may be from the environment and soil in which the food stuffs were cultivated or environment in which they were marketed. Soil, environment and air may have been contaminated due to certain factors such as organic waste, refuse burning, industrial effluences, transport and power generation. The concentrations of heavy metals in selected food stuffs were observed to be higher than the WHO/SON 2012 standard and thus may poss serious health issue so more heavy metals on these selected food stuffs should be conducted to ascertain the level of pollution.

3. Polycyclic Aromatic Hydrocarbon

The result showed that all the selected food stuffs were contained certain levels of PAHs except the selected fruits which the levels of PAHs were not detectible. The trend of contamination followed carrot>walnut>utazi. The levels of PAHs not detectable in apples may be as a result of the analytical method used or may be due to the environment or soil in which they were cultivated. The area's most have been free from activities that yields PAHs which may in turn contaminate plants and soil.

Carrot was shown to have the highest levels of PAHs though not above the permissible limit of 0.01mg/kg to 0.1mg/kg as prescribed by WHO and SON. Here in Nigeria, carrots are cultivated in northern states and a lot of activities may be going on there which may yield PAHs in the environment for instance, for a while now a lot of bomb explosion as been occurring and this may also generates PAHs in the environment which may be the cause of high levels of PAHs in carrot cultivated there. Contamination may also have resulted due to air pollution from car exhause, and the environment in which carrots were sold due to the fact that carrot has very light skin and chemicals can easily penetrate through them and the grow as root so can easily absorbed chemicals from soil.

The selected food stuffs may have been contaminated with PAHs through pollution in irrigation water, farm soil or due to pollution from the highways traffic and air in our environment and this may also have affected the nutritive values of the food stuff (Mohammed and Khairia, 2012).

4. Relationship between Heavy Metals and Proximate Contents

There was very high positive significant correlation between Cr and TPAH ($r = 0.904$) and Ni ($r = 0.875$); Cd and Ni ($r = 0.782$) and Cr ($r = 0.9$); Pb and TPAH ($r = 0.860$), Ni ($r = 0.971$), Cr ($r = 0.964$) and Cd ($r = 0.868$); Moisture and Mn ($r = 0.86$); Ash and TPAH ($r = 0.976$), Cr ($r = 0.797$) and Pb ($r = 0.76$); Protein and Cu ($r = 0.771$) and crude fibre ($r = 0.987$).

There was very high negative significant correlation between Lipid and Moisture (r = -0.737); Crude fibre and Moisture (r = -0.878); Protein and Moisture (r = -0.86).

There was high positive significant correlation between Ni and TPAH (r = 0.771); Cd and TPAH (r = 0.632); Ash and Ni (r = 0.683) and Carbohydrate (r = 0.548); Crude fibre and Cu (r = 0.677) and Lipid (r = 0.575)

There was high negative significant correlation between Mn and Cu (r = -0.651); Lipid and Mn (r = -0.61); Crude fibre and Mn (r = -0.55) and Carbohydrate (r = -0.53); Protein and Mn (r = -0.54) and Carbohydrate (r = -0.53).

5. Relationship between Food Stuffs

All the food stuffs showed very high positive significant correlation as indicated between Red apple and Utazi (r = 0.972); Green apple and Utazi (r = 0.973) and Red apple (r = 0.986); Walnut and Utazi (r = 0.908), Red apple (r = 0.877) and Green apple (r = 0.852); Carrot and Utazi (r = .970), Red apple (r = 0.989), Green apple (r = 0.99) and Walnut (r = 0.883).

V. Conclusion

The study showed that the selected food stuffs are very rich in nutrient status most especially in moisture content in all the samples and crude fibre and protein in walnut.

Concentrations of heavy metals in the selected samples were significantly higher than the permissible limit by WHO and, SON and so may pose serious adverse health concern for consumers. The Selected food stuffs are only contaminated with PAHs and do not pose serious adverse health concern.

Food stuffs should be evaluated regularly to avoid serious pollution of these food stuffs by heavy metals and PAHs. Also eating raw or unprocessed food stuff should be discouraged by relevant health authorities.

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