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Speciation of First Row Transition Elements in Carrot Tubers Grown in Northern Nigeria

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Abstract This study was carried out to estimate the metal concentration and bioavailability of heavy metals in carrot grown in Jos and Kaduna. These places were chosen because of the industrial activities, high population and bomb explosions, which are well known to contribute to heavy metal pollution. The sample were collected from Monday market Kakuri in Kaduna state and Bassa Jos in Plateau state. Carrot samples were analyzed for Cu, Fe, Zn, Cr and Mn by extracted using sequential extraction method in order to determine the bioavailability of chemical forms of metal species in carrot. The metal specie concentrations were quantified using Atomic Absorption spectrometer (AAS). Results revealed that pH values ranged from 6.5 to 6.8, electrical conductivities were the same 172 µS/cm, while mean bioavailable fractions were 11.36, 95.13, 35.6, 3.8 and 13.52 for Jos and 9.15, 64.46, 20.56, 1.85 and 8.99 for Kaduna. The bioavailable fractions were very high compared to non-bioavailable fraction. Carrots from the both towns, showed low risk of Cr. Carrots from Jos showed highest values of RAC with Fe being the riskiest metal while most metal in Kaduna showed high risk. There was a case of medium risk for Mn in carrot from Jos and Kaduna respectively. According to the model used in this study the consumption of carrots from this state could present a great health risk given the bio accumulative and toxicity behavior of some metals in this study.

Keywords Bioavailability, Metal species, Toxicity, Root crops, Soil, heavy metals, Risk assessment

Introduction

Carrot is largely cultivated in the Northern part of Nigeria such as Zaria, Sokoto, Kano and Jos. Carrot, scientifically called Daucus carota is a root vegetable with a range of colours like orange (mostly), purple, red and yellow. It contains mostly the tap root which is mainly eaten and the green leafy part which is eaten as well but it's not common and is always crispy when Fresh [1]. It grows well in Sandy soil free from stones and lumps and it is planted in rows at least 3-4 inches apart on a raised bed, at about 1-3 weeks, it begins to germinate and can be harvested at any size but has a better flavour when it has turned bright orange [2]. It is a good source of vitamin A, C and K and thus generally considered highly nutritive.

In recent years, the consumption of carrot and its product have increased steadily due to their recognition as an important source of natural antioxidant besides the anticancer activity of beta carotene being a precursor of vitamin A [3].

Though carrots are grown in a sandy soil free of stones and lumps, the top soil on which the crop grows is made up of heterogeneous material such as decomposing plants and animals, inorganics, clay and slit particles solutions and mixture of gaseous substances [4]. Soil is exposed to atmospheric decomposition from various human activities and natural sources and that has earned soil a general name sinks and source of pollutants by researchers [5].

The term "Speciation" is the process of identification and qualification of different format or phases in which one element is present in a material [6]. Speciation is the surest method of assessing toxicity of a substance because not all forms of a substance in a media are available for absorption or uptake [7]. However various extraction methods exist including single and multiple extraction method which are being applied on every segment of the environment [8].

Over the past 20 years, studies of chemical speciation have been presenting great relevance, leading to the development of various methods of analysis used in areas of health, food quality control and environment [8]. Transition element also known as transition metals are any element in the d-block of the periodic table which includes group 3-12 on the periodic table, therefore according to IUPAC transition metals are element whose atom has a partially filled d sub-shell or which give rise to cations with an incomplete d sub -shell [9].

Transition metals are heavy metals. Heavy metals are considered serious pollution because of their toxicity persistence and non-biodegradable condition in the environment thereby constituting a threat to human beings and other forms of biological life [10]. Plants absorb minerals element from soil and accumulate same in tissues of roots and shoots at various levels of concentration [13]. Other sources of contamination of plants by heavy metals include: rain in atmospherically polluted areas, release from vehicles can accumulate in surface of the soil and their deposition over time can lead to abnormal enrichment, thus causing metal contamination of surface soil [12].

Cultivation of carrots is one of the major sources of income for many northern farmers. Since the beginning of bomb explosions in the area, land degradation and the fear of being killed by bombing have caused a decline in agricultural products thereby making agricultural activities less attractive. Heavy metals found in bomb have been reported to be source of concern as an impurity to crops. Information is yet to be known about the level of contamination. The risk of intake of crops grown in this area have not been investigated, therefore the focus of this research is to identify the heavy metals in carrot and to determine their fractions in the crop. The selected vegetable is known to consume by both children and adults. Therefore, this shows a great interest in the level of heavy metals in this vegetable could be achieved as the result of bomb blast which is rampant in that area. The study draws heavily on the fact to investigate contractions of Fe, Cr, Zn, Cu and Mn.

The study aimed to identify and quantify the various species of selected first row transition metals found in carrot grown in Northern Nigeria with the objectives to determine the physicochemical properties of carrot and speciation of the metals. The determination of the level of iron, chromium, zinc, copper and manganese in carrot grown in northern part of Nigeria will be used to sensitizing the general population of Nigeria on the importance of environmental conservation. The study will also inform the authorities charged with environment management on the level of heavy metals in carrots grown in northern part of Nigeria hence providing a reference for future studies. The results from this study will be used to determine the remedial action to be taken to avoid toxicity on the people.

Carrot is one of the important root vegetable rich in bioactive compounds like carotenoids and dietary fibers with appreciable level of several other functional components having significant health promoting properties. The consumption of carrot and its products is increasing steadily, due to its recognition as an important source of natural antioxidants have anticancer activity [14]. Apart from carrots being traditionally used in salad, these could commercially be converted into nutritionally rich processed products like juice, concentrate, dried powder and canned.

Carrots are good source of carbohydrate and minerals like Ca, P, Fe and Mg [15]. The chemical composition and constituents of carrot as moisture (86%), protein (0.9 %), fat (0.2 %), carbohydrate (10.6 %), crude fiber (1.2 %), total ash (1.1 %), Ca (100 g) and P (100 g) [16]. The edible portion of carrot contains about 10 % carbohydrates having soluble carbohydrate ranging from 0.8 to 1.1g [17]. Carrots contains 1.67-3.35 % reducing sugar, 1.02-1.18 percent non reducing sugar and 2.71 - 4.53 percent total sugars in six cultivars of carrot. The reducing sugar accounted for 6-32 % of free sugars in four hybrid varieties of carrot. The free sugars identified are sucrose, glucose, xylose and fructose [18]. The carrot root contains appreciable amount of Thiamine, niacin, folic acid, riboflavin and vitamin C [19]. The taste of carrot is mainly due to the presence of glutamic acid and the buffering action of the free amino acids [20].

Speciation is a process of identification and qualification of different forms or phase in which one element is present in a material [6]. Speciation involves single and sequential extraction; these methods are used widely for investigation of soil, water sediment and very important but hardly mentioned foods, providing information on the mobility and availability of metals and elements [21]. Single extraction reagents (usually binder, acid or diluted salt) are used to treat the sample and the measurement is made on the number of elements of interest that are released from the matrix [22].

In sequential extraction, a detailed insight into the properties and behavior of the elements can be accessed. Reagents with different chemical properties are used so that the chemical forms of an element can be leashed out by various mechanism, like complexation or acidification [22]. This process is more time consuming than simple extraction because it provides a separation of the total content of an element in fractions with different bioavailability while the first fraction is unstable and thus readily available for absorption, the last fraction is characterized by its reduced mobility [23].

Sequential extraction consists in the use of number of extractors with different chemical properties that are progressively applied in a sample. Most of sequential extraction scheme include different group of extractors. Extractors with ion exchange properties, extractors with dissolution of carbonates properties, extractors with acid reducing properties, extractors that weaken the metal with organic compounds and sulfides extractors which promote the dissolution of silicates and minerals [24]. To understand the mechanism involves between the chemical forms and extractors such as mobility and bioavailability associated to these elements, it is necessary to know each phase corresponding to sequential extraction. The confirmation of the concentration of trace toxic and those considered essential nutrients in food elements is performed in many countries.

In the period of ten years, it has been shown that food safety and nutritional quality of foods also depend on the chemical form in which an element is present therein, since the bioavailability, activity and toxicity of beneficial minerals are a function of metal concentration, it's oxidation state and the chemical form in which it is found in the samples [34].

The number of studies on chemical speciation in food has increased significantly but only few elements are widely studied. Element such as Co, I, Mn, Fe, Zn, Cu and Cd have received little or no attention so far because of their low concentration in foods, complex instability and chemical behavior of the species making it a challenge for the chemistry [32].

Heavy metal pollution in soil refers to cases where the quantities of the elements in soil are higher than maximum allowable concentration and this is potentially harmful to biological life in such location [11]. Heavy metals occur at typical background in all ecosystems however, anthropogenic releases can result in higher concentration of these metals relative to their normal back ground values hence the pollution [11]. Heavy metals released from vehicular emission can accumulate in surface soil and their deposition overtime can lead to abnormal enrichment, thus causing metal contamination of surface soil [35]. The toxicity and mobility of heavy metals in soil depends not only on the total concentration but also on their chemical form, bonding state, metal properties, environmental factors, soil properties and organic matter content [36]. Exposure of children, generally accepted as the highest risk group who have a higher absorption rate of heavy metals because of their active digestion system and sensitivity of haemoglobin, to heavy metals can greatly increase ingestion of metal laden soil particles via hand to mouth activities. In addition, adults may be exposed to threat since inhalation is easier pathway for toxic metals to enter their body [35].

Materials and Methodology

Study Area

This samples for this study were carried out in Kaduna and Jos. Geographically both are northern towns. Kaduna lies within the latitude 10°36'33.5484"N and longitude 7°25'46.2144"E and shares boundary with Abuja and is known for their textile, petroleum, steel and metal production, with a population of about 800,000. Kaduna is inhabited by the Hausas, mostly Muslims. It is a center of education, with a large military academy and few collages of education. There are not many landmarks or tourist attractions in the city. On the other hand, Jos lies within the latitude 9°53'47.4972"N and longitude 8°51'29.9916"E sharing a common boundary with Kaduna. Mining activities are popular in Jos for tin and coal mining. With a population of about 900,000 people and beautiful sceneries, cool climate and highlands, Jos is known as a center of tourism with great number of travelers who come to see local land marks [26].

Sample Collection

Sample of carrots were collected from Kakuri in Kaduna south and Bassa in Jos. In Kakuri, four different directions, north, south, east and west were mapped out. Five carrots tubers were collected from different local farms along each direction to give 20 carrot tubers. All four directions were pooled together and five carrot tubers collected from each direction to produce 20 tubers from Kakuri. The same procedure was repeated at Bassa in Jos and a total of 40 carrot tubers were transported for two days three days and taken to the Chemistry laboratory at Imo state laboratory for analysis.

Preparation

As advised by the farmers samples were only washed when analysis was to begin. The samples were gently washed under running tap water to remove adhered soil particles and then rinsed with distilled water. The samples were air dried to remove residual moisture. Each air-dried sample was blended to a past and was sieved to obtain fine texture was which was stored in an airtight container awaiting analysis.

Figure 3a: Carrot sample from Kakuri

Figure 3b: Carrot samples Bassa

Physicochemical Analysis

The carrot physicochemical analysis was determined according to the method of Enyoh *et. al*, 2017 [48]. The electrical conductivity was measured after calibration with KCl using HANNA HI8733 EC METER in S/cm. 10 g of the air-dried carrot sample was carefully weighed into the beaker and 50ml of distilled water was added. It was then shaking vigorously. The EC probe was then introduced into the carrot water suspension for 60seconds and the reading was taken. The pH was determined using JENWAY 3510PH METER which was calibrated using buffer 4 and buffer 7 by dissolving one capsule each in 100ml water respectively. The pH was determined also with the same method used for the EC measurement [36, 37].

Metal Speciation Analysis: Two grams of each powered sample was weight out and transferred in a 50 ml tube of polypropylene for centrifuge and extraction was done according to the processes. Water soluble fraction (F1): Two grams of the meshed sample was extracted with 20 ml of deionized water for 2 hours. Exchangeable fraction (F2): Into the residue of F1, 20 ml of 1mol of $MgCl_2$ was added and the PH adjusted to 7 and the mixture was allowed for an hour. Carbonate bound fraction (F3): 20 ml of 1 Mol of NH_4AOC at pH 5 was added into F2 residue and the mixture was allowed for five hours before extracting. Fe-Mn Oxide bound fraction (F4): Residue from F3 was extracted with 20ml of 0.04 mol $NH_2OH.HCl$ in 25% HOAC at 90°C and agitated intermittently. Organic bound fraction (F5): 15 ml of 30% H_2O_2 was added to F4 residue and PH adjusted to 2 using nitric acid and allowed for five and half hours at 85°C water bath. After cooling 5ml of 3.2 mol NH_4OAC in 20% HNO_3 was added and shaken for 30 minutes before final dilution to 20ml with deionized water. Residual Fraction (F6): Residue from F5 was digested using a HCl digestion procedure and was allowed to stand for 30 minutes [26,27,28,36].

Atomic Absorption Spectrometry (AAS): The metal concentrations of the carrot samples extracts were detected in triplicates with atomic absorption spectrometry (AAS) using a Perkin Elmer A Analyst 800 atomic absorption spectrometry.

Data Analysis: Using SPSS (Statistical package for social sciences) version 18.0 the mean, standard deviation and level of significance were analyzed, and results were reported as mean ± standard deviation. Sum of fractions for each metal was ∑F(X) were obtained and used as metal concentration in chemometric methods.
Bioavailability (BA) was quantified using the expression:

$$BA = \frac{F_1 + F_2 + F_3}{F_1 + F_2 + F_3 + F_4 + F_5 + F_6} \quad \text{..........1}$$

where $F_1 + F_2 + F_3$ represents the most mobile fraction and summation $F_1 + F_2 + F_3 + F_4 + F_5$ represent the metals concentration in the sample.

According to Verla et al., 2017 the most available metal fraction $F_1 + F_2 + F_3$ constitute the risk of each metal, called risk assessment code (RAC).

Results and Discussion

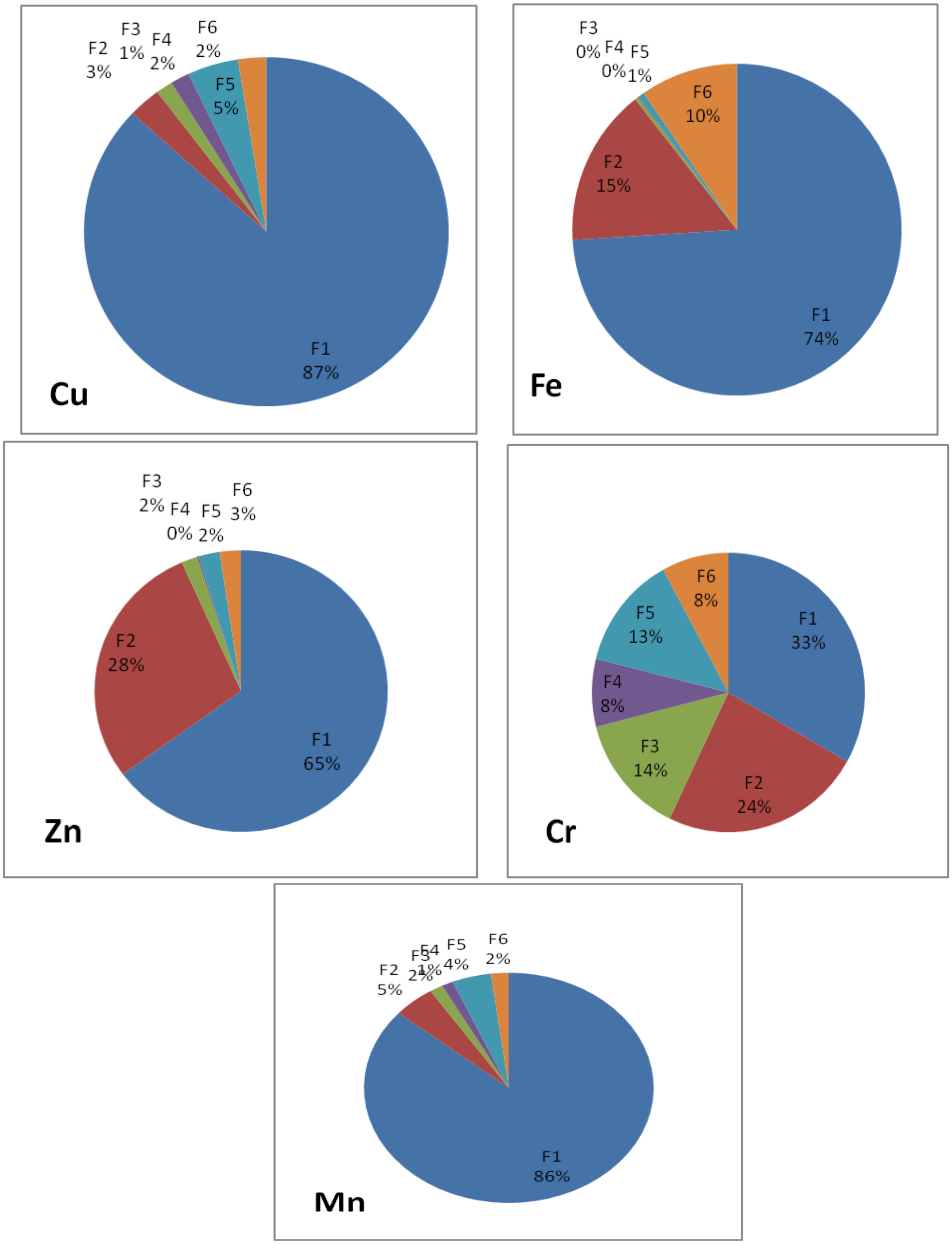
Table 1: Physicochemical properties of carrot samples

Parameter	Jos	Kaduna	Mean
Ph	6.8	6.5	6.65
EC	172µs/cm	172µs/cm	173µs/cm
Eye colour observed	Orange to white	Orange to white	-
Odour	Carrot smell	Carrot smell	-

Table 2: Heavy Metal Fraction in Carrot Sample

Carrot	Metal	F1	F2	F3	F4	F5	F6	∑F(x)	Mean	SDV
Jos	Cu	10.812	0.364	0.186	0.213	0.561	0.311	12.447	2.075	4.23
	Fe	78.462	16.31	0.365	0.115	0.600	10.17	106.02	17.67	36.06
	Zn	24.32	10.61	0.67	0.068	0.870	0.884	37.442	6.24	12.73
	Cr	1.776	1.28	0.746	0.418	0.705	0.426	5.351	0.891	1.82
	Mn	12.631	0.681	0.217	0.188	0.640	0.291	14.647	2.441	4.98
Kaduna	Cu	8.24	0.721	0.194	0.361	0.684	0.426	10.626	1.771	3.62
	Fe	57.62	3.418	3.422	0.217	0.558	0.741	65.976	10.99	22.42
	Zn	16.47	3.446	0.645	0.471	0.726	2.428	24.186	4.028	8.22

Cr	0.861	0.672	0.321	0.337	0.219	0.336	2.746	0.457	0.93
Mn	8.471	0.318	0.206	0.21	0.526	0.500	10.233	1.706	3.48



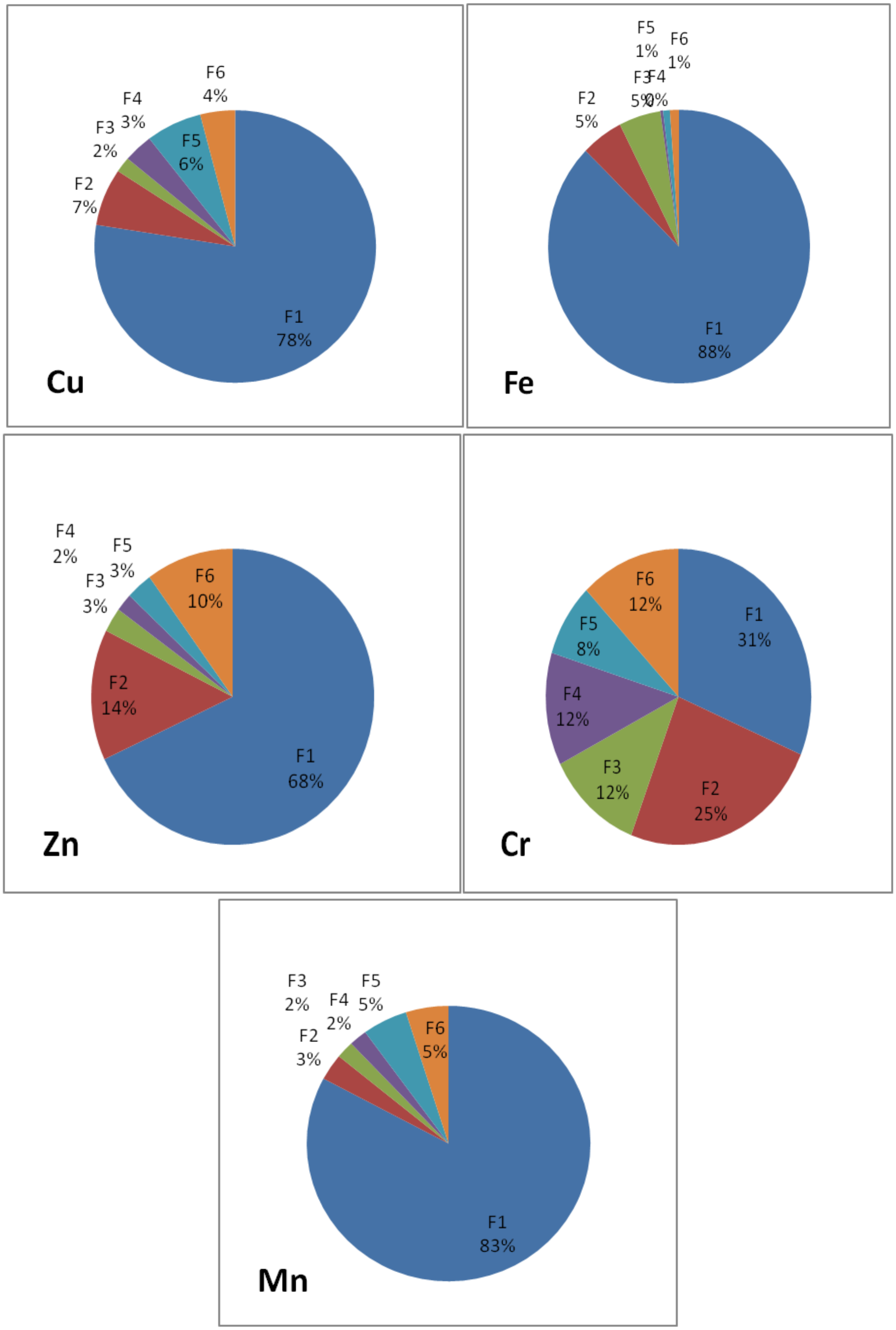

Cu
F1 78%
F2 7%
F3 2%
F4 3%
F5 6%
F6 4%
Fe
F1 88%
F2 5%
F5 1%
F6 1%
Zn
F1 68%
F2 14%
F3 3%
F4 2%
F5 3%
F6 10%
Cr
F1 31%
F2 25%
F3 12%
F4 12%
F5 8%
F6 12%
Mn
F1 83%
F2 3%
F3 2%
F4 2%
F5 5%
F6 5%

Table 3: Bioavailability of Metal

Carrots	Metal	Bio Fraction ∑(F1+F2+F3)	Non-Bio ∑(F4+F5+F6)	Residual (F5)	RAC (%)	Significance
Jos	Cu	11.362	0.774	0.311	1,136	High risk
	Fe	95.137	0.715	10.16	9,510	High risk
	Zn	35.6	0.938	0.884	3,560	Low risk
	Cr	3.802	1.13	0.426	380	Medium risk
	Mn	13.526	0.828	0.291	1,380	High risk
Kaduna	Cu	9.155	1.045	0.426	915.5	High risk
	Fe	64.46	0.775	0.741	6,446	High risk
	Zn	20.561	1.197	2.428	2,056	Low risk
	Cr	1.854	0.556	0.336	185	Medium risk
	Mn	8.995	0.736	0.500	891	High risk

Discussion

The samples collected from Jos and Kaduna were analyzed for the physicochemical parameters which involves the pH, electrical conductivity, smell and heavy metal concentration of each sequential extract referred to simply as metal fraction. Physicochemical characteristics of carrot gotten from the two states are shown in table 1. The pH of the carrots from the two states ranged from 6.5 to 6.8. This agrees to the pH values of carrots which is between 6.0 to 6.8 [49]. If the carrots are slightly outside this range or between 5.5, it is too acidic. So therefore, the carrots from this area were found to be neutral. The carrots from the two states showed the similar electrical conductivity which is 172 µS/cm for both. The EC values indicate ionic concentration of the carrot. The EC level is a good indication of the amount of nutrient available in the carrot. The Eye colour observed during the extraction was the change of the original carrot colour which is orange colour to white after extracting with F1 to F6. The scent of the carrot sample after extraction remained the same as the original carrot smell.

Heavy Metal Fractions in Carrot Samples

Table 2 shows the concentrations of Cu, Fe, Zn, Cr and Mn in carrots from Jos and Kaduna. The carrots from Jos and Kaduna seems to have a high concentration of Fe (106.02 mg/kg and 65.97 mg/kg) respectively and lower concentration of Cr (5.35 mg/kg and 2.76 mg/kg). The heavy metal concentration in the carrots shows different variation. The order of abundance of the analyzed metals from carrot in Jos site was Fe > Zn > Mn > Cu > Cr and carrot from Kaduna Fe > Zn > Cu > Mn > Cr. The mean concentration (mg/kg) of metal species are shown in Table 3.2. Results of speciation analysis revealed highest value of mean concentration of metal species to be Fe (17.67 mg/Kg) carrot from Jos while carrot from Kaduna Fe (10.98 Kg/mg) but the mean concentration of Cu in carrot from Jos was a slightly higher than the carrot from Kaduna. Chromium is one of those heavy metals in environment whose concentration is steadily increasing due to industrial growth, especially the development of metals, chemicals and tanning industries [11]. The most common forms of chromium are chromium VI and chromium III [41]. Chromium III is an important component of a balanced human and animal diet and its deficiency causes disturbance to glucose and lipid metabolism in human while chromium VI is carcinogenic [42]. Although chromium toxicity in the environment is rare, it still prevents some risks to human health since chromium can be accumulated on skin, lungs, muscles fat, in liver, dorsal spin, hair, nails and placenta where it is traceable to various health conditions [11]. Cr detected in Kaduna sample was very low in concentration in both samples. This shows carrot from Jos had a high metal concentration than the carrot from Kaduna.

Zinc is an essential trace element for plants, animals and human found in virtually all food and portable water in the form of salts or organic complexes [46]. The average adult body contains between 2-3g of zinc [46]. Zinc is used to form connective tissue like ligaments and tendons. Zinc toxicity is rare but concentration of up to 40mg/l, it may induce toxicity characterized by symptoms of irritability, muscular stiffness and pain [47].

Bioavailability of Metals in Carrot

95.13 mg/Kg of Fe was found to be bioavailable for human consumption in carrot from carrot from Jos and 64.46 mg/Kg of Fe in carrot from Kaduna. The highest concentration of Fe was observed from the carrot. Fe is an important mineral found in animal and human. Most of the Fe found is located in red blood cells as part of the haemoglobin. Fe in excessive doses can lead to iron poisoning or toxicity.

The mean concentration of Zn tested in the ranges from 24.18mg/kg, with the carrot from Jos having the highest concentration of Zn. bioavailable Zn in the tested sample ranges from 20.56 mg/Kg to 35.6 mg/Kg with carrot from Jos having the highest bioavailable fraction of Zn in the carrot sample from the two states. However, it is observed that the level of bioavailability of Zn in the samples was below the permissible limit of 100.00 mg/Kg of Zn for food by WHO/FAO and it is not acceptable as it is an indication of Zn deficiency. Zn is an important element for both plants and animals, it plays an important role in several metabolic processes, it activates enzymes and it is involved in protein synthesis and in carbohydrates nucleic acid and lipid metabolism [12]. However high concentration of Zn can result to damage of the pancreas, disruption of protein metabolism and arteriosclerosis. The concentration of Mn is observed to be high in the carrot from Jos having the concentration of 13.5 mg/Kg and 8.99 mg/Kg from carrot from Kaduna. 11.36 mg/Kg of Cu was found bioavailable for human consumption. Besides other important functions, Cu is use as a co factor of many enzymes, maintenance of healthy nervous system, protect against anaemia and influence the proper functioning of Zn and Fe in metabolism [12]. However, research has shown deleterious effects due to high amounts of Cu in the body to the extent that kidney and liver damages are traceable to elevated copper concentration. From the results the levels of Cr were found to be lowest in the samples. Table 3 shows concentration of bioavailable Fe in the carrots. The mean concentration of Fe in the carrot samples ranges from 10.98mg/kg to 17.67mg/Kg. It was observed that the level of Fe recorded in the sample were above the permissible limit, therefore constituting a matter of concern.

Manganese is essential for normal physiological functional of humans and animals and exposure to low levels of manganese in the diet is considered nutritionally essentially in humans. However chronic exposure to higher doses is detrimental to human health [43]. In higher doses manganese is toxic and its toxicity varies with route of exposure, chemical species, age, sex and animal species [44]. The nervous system has been determined to be the primary target organ with neurological effects generally observed [43]. Syndrome called manganism may result from chronic exposure to higher levels of manganese [44]. Manganism is characterized among other symptoms, weakness, tremors, masklike face and psychological disturbance [45, 48, 49].

Risk Assessment Code

The model assumes that the most bioavailable fraction is likely to be absorbed into the body system hence cause toxicity to the consumer. Therefore, summing the first three fractions and expressing them as a percent risk is the basic tenet of RAC. Five categories are employed in the interpretation of the model results in figure 11 as follows; no risk: RAC>1, low risk: 1<RAC>10, medium risk: 11<RAC>30, high risk: 30<RAC>50, very high risk: RAC<50. There was low risk of Cr from carrots in both states. Carrots from Jos showed highest values of RAC with Fe being the riskiest metal. Most metals in Kaduna showed high risk. There was case of medium risk in Mn from carrot from Jos and Kaduna respectively. The order of decreasing risk associated with consuming this carrot is Jos >Kaduna. The concentrations of heavy metals in plants largely depend on the concentrations of heavy metals in the soil. The content of heavy metals in soil was not evaluated in this study but could be a reflection of the metal concentrations in the carrots.

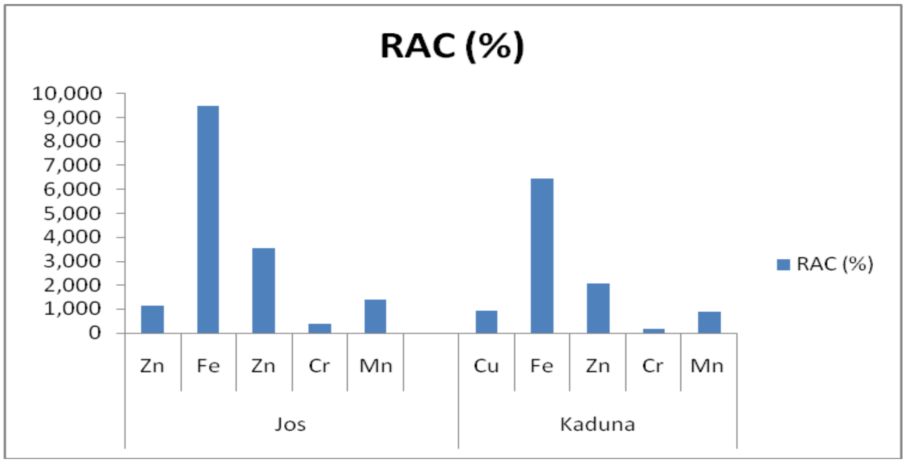


Figure 11: Bar chart Comparing the RAC (%) of carrot samples from Kaduna and Jos

Conclusion

The pH of the carrots from the studied section of speciation of first row transition element in northern part of Nigeria were found to be neutral and below the recommended pH for carrots. The heavy metals analyzed were Cu, Fe, Zn, Cr and Mn. Carrots from Jos showed high level of concentrations of metals when compared with carrot from Kaduna, these may be related to the high level of coal mining and tin mining, high population density and bomb explosion in Jos. On the basis of RAC, Fe was revealed to be most risky of all metals and like everything else when in excess can pose a health risk. Therefore, consumption of carrots from the state should be in moderations rather than excessive.

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