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COMPARATIVE STUDY ON MINERAL ELEMENTS AND HEAVY METAL COMPOSITION OF ALLIUM SATIVUM CLOVES (NIGERIAN /INDIAN SPECIES) AND COSTUS AFER (KER GAWL) LEAF BY INDUCTIVELY COUPLED PLASMA-OPTICAL EMISSION SPECTROMETER (ICP-OES).

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ABSTRACT
The present study aimed at investigating two commonly and extensively used herbs namely *Costus afer* (ginger lilly) and *Allium sativum* (garlic) for their essential element and heavy metal composition and also to compare the Nigerian specie of *Allium sativum* to that of Indian species for their metal composition using a highly sensitive Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES). Eighteen minerals elements (Ba, Be, Bi, B, Ca, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Se, Ag, Sr, V and Zn) and three heavy metals (As, Cd, Pb) concentration were determined for the first time in *C.afer* and *A.sativum*. Wet digestion method using a mixture of 2ml of concentrated HNO_3:$HClO_4$ (4:1 v/v), 1ml H_2O_2 and 1ml miliQ water was used for digestion of the samples using microwave in a Microwave Digestion System (MDS) and analyzed by ICP-OES. The results obtained revealed the following concentration of metals in *C.afer* leave in mg/kg dry weight: B= 18.36; Ba= 53.52; Bi=2.10; Ca=1017.42; Cd=0.42; Cr=0.18; Cu=6.66, Fe=303.66; Mg=4386.6; Mn=808.80, Mo=0.84;N=7.14, Pb=1.80; Sr=32.16; V=1.68 and Zn=24.24 while that of the Nigerian/India garlic cloves were B=2.72/1.54 ; Ba= 11.24/4.86; Bi=0.072/0.216;Ca=47.20/34.93; Cd= 0.036/ND; Cu= 2.69/1.67, Fe= 27.94/20.64; Mg=312.6/240.84; Mn=3.9/4.08, Mo=0.24/0.17;Ni=0.65/0.77, Pb=0.14/0.22; Sr=2.57/2.24; V=0.144/0.024 and Zn=8.59/8.32. Ag= As=Be=Co=Se were below the detectable limit in both *C.afer and A.sativum*, Cr was detected only in the *C.afer*. In conclusion, the concentrations of the essential element detected were higher in the *C.afer* leave than in garlic cloves in virtually all elements. The number of mineral element below detectable limit was same in both *C.afer* and *A.sativm*. Comparing the Nigerian and Indian garlic, there was no significant different between the elemental composition. In general, the levels of metals in the analyzed *C. afer* leaf and garlic cloves samples were found below the FAO/WHO maximum permissible limit; hence they are safe for human consumption and can be considered as a good source of essential nutrients.

KEYWORDS: Ginger lilly, garlic, ICP-OES, essential elements, Heavy metal, MSD.

INTRODUCTION
Medicinal plants are the richest bio-resource of drugs for traditional medicines, modern medicines, nutraceuticals as well as chemical entities for synthetic drugs.[1] In nature, plants encompass a wide range of therapeutically valued bioactive compounds widely used in both traditional and modern therapies for improving human health with relatively less or no side effects. Globally, various medicinal plants have been well explored to discover novel drug molecules to combat the threat of ever increasing human diseases.[2–4] Pollution of foods by heavy metals which are non-biodegradable and also bio-accumulate in living tissues through food chain is a worldwide phenomenon. Studies have revealed that fruits and leafy vegetables are vulnerable to heavy metal contamination from soil, wastewater and air pollution[5-6] and as such serve as the pathways by which heavy metals enter the human tissues through ecosystem and thus leading to deterioration of health.[7]

The plant *C.afer* Ker gawl (Zingiberaceae) is among the 150 species of the genus Costus.[8-9] It is commonly called bush cane, ginger lily or spiral ginger. *C.afer* is well known to locals and locals having identified its potentials have employed it in so many health conditions. Among the previous studies carried out on different parts of *C.afer* are phytochemical composition and antioxidant activities of stem.[10-11] pharmacological activity of the aqueous leaf extract[12-13], hepatoprotective, nephroprotective and antioxidant potential of the aqueous leaf extract[13-14], antimicrobial, anti-inflammatory[15-17] of the leaf and stem, hypolipidemic effect and anti-nociceptive property[18] among others.

Garlic (*A.sativum* L.), is the second most important *Allium* crop next to the onion (*Allium cepa* L.), it is cultivated worldwide and consumed by almost every culture as a popular condiment.[19] Garlic has been used throughout history for both culinary and medicinal purposes.[20] *A.sativum* L. has a long folklore history as a treatment for cold and flu symptoms through immune enhancement and exhibits anticancer, antioxidant, anti-inflammatory, antimicrobial, antithrombotic, hypocholesterolemic, hypoglycemic, and hypotensive activities. And it is used to treat diabetes, atherosclerosis, hyperlipidemia, thrombosis and hypertension. Also, it acts against stroke, gastrointestinal, neoplasias, antiplatelet action etc.[21-22]

Many analytical methods are available for the determination of trace elements in plant material such as AAS but these methods require the decomposition of the sample.[23-24] Sample preparation is a critical step for the analysis of metals due to presence of different type of matrices but with the advancement of technology such as MDS, digestion is now rapid and is an efficient method for sample digestion prior to the determination of trace metals.[25-26] Moreover, ICP-OES is one of the most accurate and latest analytical techniques for the determination of trace elements in numerous sample types.

The phyto-constituents, yield, elemental and mineral composition of different plants depends on the activity and medicinal properties embedded in the plant which is a factor of both the geographical and other environmental influences on the plant.[27] However, most studies on *C. afer* and *A.sativum* centered more on their medicinal values with little or no attention on their metal composition. Before the commencement of this work, there were no comprehensive literature reports on the metal composition of Nigeria *A.sativum* L. (garlic) and *C. afer* ker gawl leave in spite of its extensive use. Literature survey shows less information on essential mineral and heavy metal composition of *A. sativum and C.afer*. With this background, we investigated the environmental influence and geographical location on essential minerals and heavy metal composition of Nigerian and Indian *A.sativum* cloves.

MATERIALS AND METHODS

Reagents

The standards for ICP-OES were prepared from stock solutions of studied elements at 1000 mg/L concentration obtained from Perkin Elmer (USA). All other reagents and solvents used in this study were of analytical grade obtained from Fischer Scientific (USA). Milli-Q water was used for washing laboratory glassware and in preparation of sample and standard solutions.

Plant material

Sample collection, identification, processing and extraction

C.afer leaf was harvested from a farm land in the University of Port Harcourt, Port Harcourt, Rivers State, Nigeria while the *A. sativum* was purchased from Choba Junction market, opposite Delta Campus, University of Port Harcourt, Rivers State, Nigeria and from vegetable shop in Lucknow India. The plant was identified and authenticated by Dr. MMA Khan, Dept. of Botany, Ashia PG College, Lucknow, India. After identification, *C.afer* leave was washed with clean tap water to removed dirt from the leaves. The leaves were shade dried in a well-ventilated place to avoid contamination by dust and then grinded into powder for the study whereas the *A. sativum* cloves was peel and a portion taken for wet digestion.

Microwave digestion

Digestion of air dried powder of *C.afer* leaf and *A.sativum* cloves was carried out using MDS (Multiwave3000, Anton Paar, Perkin Elmer) with the Rotor 16HF100 (100 ml PFA vessels, 40 bar) and Pressure, Temperature (P/T) sensor. About 0.1and 0.5g of powdered *C.afer* leaf and fresh *A.sativum* cloves respectively was digested with 2.0mL HNO_3:$HClO_4$, 1.0 ml of $H_2O_2$and 1.0 ml of miliQH_2O in microwave digestion system, according to the digestion program presented in Table 1. The resulting clear solution was cooled and diluted to 12.0 mL with Milli-Q water.

Table 1: Operating conditions for the MDS.

S. No.	Power [W]	Ramp [min]	Hold [min]	Fan
1	400	5	10	1
2	800	5	10	1
3	0	0	10	3

ICP-OES analysis: The calibration standards for ICP-OES were prepared by diluting the stock standard solution (1000 mg/L) in 0.2% (v/v) nitric acid. Working solutions were prepared from the stock as necessary. The calibration curves for all the studied elements were prepared by different concentrations of standards in the range 0.005 mg/L to 1.0mg/L from working solution (Figure 1). The above clear solution obtained after microwave digestion was analyzed by ICP-OES (Optima 8000, Perkin Elmer) for elemental analysis with following operational conditions (Table 2).

Table 2: Operating conditions for the ICP-OES.

Operating Condition	Value
Plasma Gas Flow (L/min)	8
Auxiliary Gas Flow (L/min)	0.2
Carrier Gas Flow (L/min)	0.55
RF Power [W]	1300
Plasma view	Axial
Sample flow rate (ml/min) 1.0	1.0

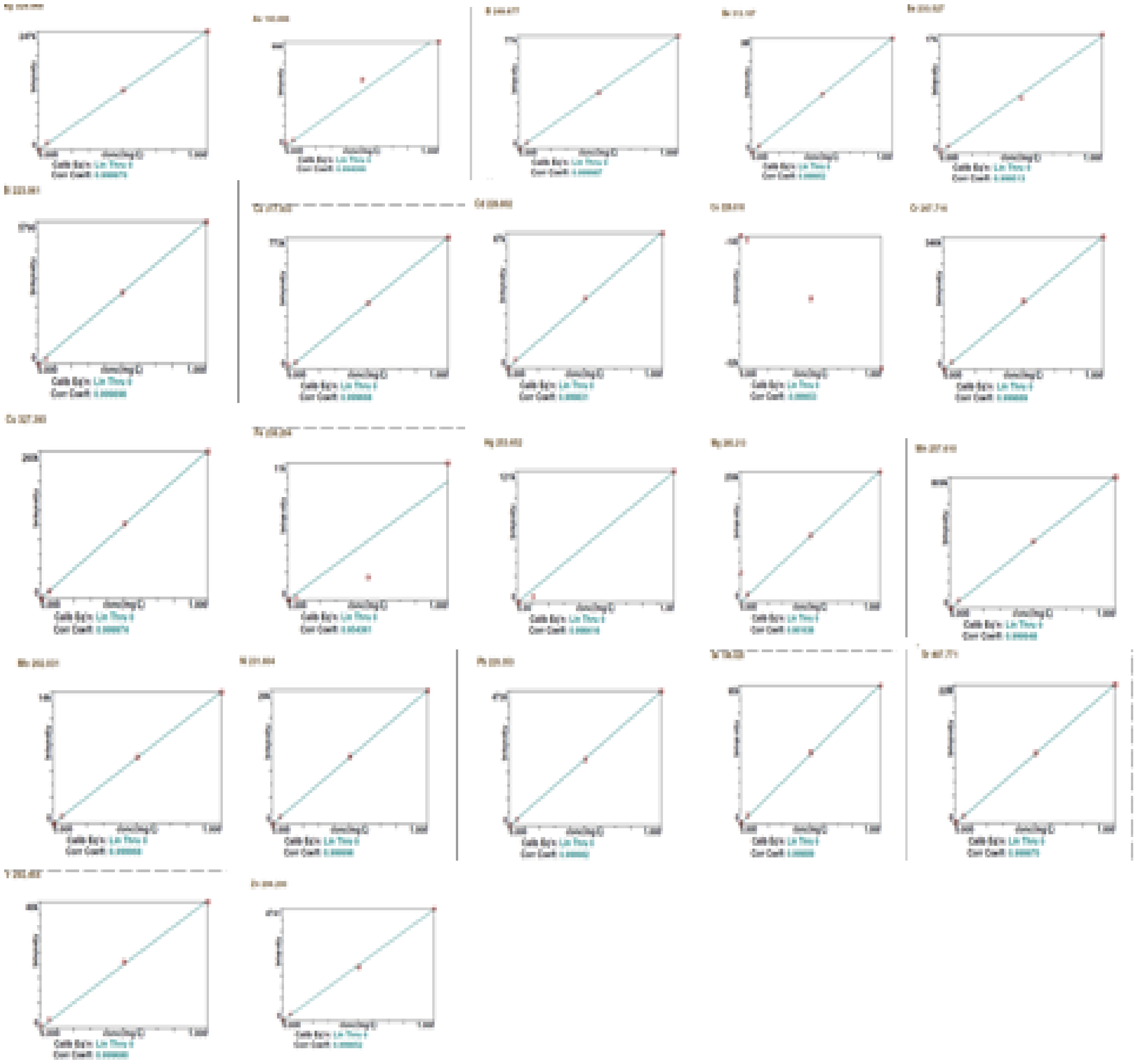

Figure 1: ICP-OES calibration curves of different element.

RESULTS

The result of the analysis showed that the elemental concentration (mg/kg) of the extract were as follows: For *C.afer* leaf, the concentration of Boron (B) 18.36 ± 0.12 mg/kg, Barium (Ba) 53.52 ± 2.88 mg/kg, Beryllium (Be) BDL, Bismuth (Bi) 2.10 ±0.3mg/kg, Calcium (Ca) 1017.42 ±62.34 mg/kg, Cobalt (Co) BDL, Chromium (Cr) 0.18 ± 0.06 mg/kg, Copper (Cu) 6.66 ±1.14 mg/kg, Iron (Fe) 303.66 ±37.62 mg/kg, Magnesium (Mg) 4386.60 ±300.0 mg/kg, Manganese (Mn) 808.80 ±19.92 mg/kg, Molybdenum (Mo) 0.84±0.24mg/kg, Nickel (Ni) 7.14 ±1.38 mg/kg, Selenium (Se) BDL, Silver (Ag) BDL, Strontium (Sr) 32.16 ± 2.16 mg/kg, Vanadium (V) 1.68 ± 0.24mg/kg and Zinc (Zn) 24.24 ± 0.96 mg/kg (Table 3). Moreover, the level of toxic metals were Arsenic (As) (BDL), Cadmium (Cd) 0.42 ±0.06 mg/kg, Lead (Pb) 1.80 ± 0.00 mg/kg (Table 3).

Nigerian/Indian *A.sativum* cloves: the concentration of Boron (B) 2.724 ± 0.25/1.536±0.26 mg/kg, Barium (Ba) 11.244 ± 5.41/4.86±0.42mg/kg, Beryllium (Be) BDL, Bismuth (Bi) 0.072±0.024/0.216±0.00, Calcium (Ca) 47.196±8.24/34.932±3.40 mg/kg, Cobalt (Co)

BDL, Chromium (Cr) BDL, Copper (Cu) 2.688±0.048/1.667±0.084 mg/kg, Iron (Fe) 27.94 ±2.45/20.64±1/.05mg/kg, Magnesium (Mg) 312.60 ±37.92/240.84±5.76mg/kg, Manganese (Mn) 3.90 ±0.42/4.08±0.72 mg/kg, Molybdenum (Mo) 0.24±0.0/0.168±0.0, Nickel (Ni) 0.648±0.072/ 0.768±0.072mg/kg, Selenium (Se) BDL, Silver (Ag) BDL, Strontium (Sr) 2.568 ± 1.10/2.244±0.06mg/kg, Vanadium (V) 0.144 ± 0.0/0.024±0.0mg/kg and Zinc (Zn) 8.592 ± 0.72/8.316±0.012 mg/kg (Table 3). Moreover, the level of toxic metals is as follows Arsenic (As) BDL, Cadmium (Cd) 0.036 ±0.012/ND mg/kg, Lead (Pb) 0.144±0.0/0.216±0.00 (Table 3).

Table 3a: Concentration (mg/100g) of different minerals in *C.afer* (CA) Ker Gawl leave, Nigeria *A.sativum* (NAS) and India *A.sativum* (IAS) cloves.

S/N	Elements	Symbol	Wave Length (nm)	Concentration (mg/100g ± SD)		
				CA	NAS	IAS
1	Silver	Ag	328.068	BDL	BDL	BDL
2	Boron	B	249.677	18.36±0.12	2.724±0.25	1.536 ±0.26
3	Beryllium	Be	313.107	BDL	BDL	BDL
4	Bismuth	Bi	223.061	2.10±0.3	0.072± 0.024	0.216 ±0.0
5	Calcium	Ca	317.933	1017.42±62.34	47.196±8.24	34.932 ±3.40
6	Cobalt	Co	228.616	BDL	BDL	BDL
7	Chromium	Cr	267.716	0.18±0.06	BDL	BDL
8	Copper	Cu	327.393	6.66±1.14	2.688±0.048	1.668 ±0.084
9	Iron	Fe	238.204	303.66±37.62	27.94±2.45	20.64 ±1.05
10	Magnesium	Mg	285.213	4386.6±300.00	312.60±37.92	240.84 ±5.76
11	Manganese	Mn	257.610	808.80±19.92	3.90±0.42	4.08 ±0.72
12	Molybdenum	Mo	202.031	0.84±0.24	0.24± 0.0	0.168 ±0.0
13	Nickel	Ni	231.604	7.14±1.38	0.648±0.072	0.768 ±0.072
14	Selenium	Se	196.026	BDL	BDL	BDL
15	Strontium	Sr	407.771	32.16±2.16	2.568±1.10	2.244 ±0.06
16	Vanadium	V	292.464	1.68±0.24	0.144±0.00	0.024 ±0.00
17	Zinc	Zn	206.200	24.24±0.96	8.592±0.72	8.316 ±0.012
18	Barium	Ba	233.527	53.52±2.88	11.244±5.41	4.86 ±0.42

BDL=below detectable limit

Table 3b: Concentration (mg/100g) of toxic/heavy metals in *C.afer* Ker Gawl leave, Nigeria *A. satium* (NAS)and India *A. sativum* (IAS).

S/N	Elements	Symbol	Wave Length	Concentration(mg/100g± SD)		
				CA	NAS	IAS
1	Arsenic	As	193.696	BDL	BDL	BDL
2	Cadmium	Cd	228.802	0.42±0.06	0.036±0.012	BDL
3	Lead	Pb	220.353	1.80±0.00	0.144±0.00	0.216±0.0

Table 4: Comparison of measured and certified values (mean ± SD, n = 3) in the CRM (ERA A Waters Company).

Elements	Certified mg kg^{-1}	Accepted limits	Measured mg/kg in CA, NAS and IAS		
			CA	NAS	IAS
As	101 ± 5.92	61.0-116	ND	ND	ND
Ca	6200 ± 7.27	5620-9440	1017	47	34
Cd	143 ± 5.60	104-182	0.42	0.04	ND
Co	232 ± 4.10	148-250	ND	ND	ND
Cr	320 ± 6.06	60.0-114	0.18	ND	ND
Cu	268 ± 4.72	204-332	6.66	2.69	1.67
Mg	2850 ± 5.51	1860-3840	4386	312	240
Mn	425 ± 9.69	324-525	808	3.90	4.08
Ni	236 ± 4.17	175-302	7.14	0.65	0.77
Pb	97.9 ± 11.3	69.3-126	1.8	0.14	0.22
Zn	130 ± 11.5	87-173	24.24	8.59	8.32
Se	127 ± 4.47	84.6-170	ND	ND	ND

ND= Not Detected, CA= *C.afer*; NAS= Nigerian *A.sativum*; IAS=Indian *A.sativum*

Table 5: Dietary Reference Intake (DRI)=Recommended Dietary allowance (RDA) and Tolerable Upper Intake Level (TUIL) of elements, compared to the average concentration of elements obtained from CA, NAS and IAS.

Elements	Average Concentration (µg/g)			Average concentration (mg/10g)			DRI (mg/day)		Estimated contribution to RDA (%)		
	CA	NAS	IAS	CA	NAS	IAS	RDA	UL	CA	NAS	IAS
As	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ag	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ba	53.52	11.24	4.86	0.5352	0.1124	0.0486	ND	ND	ND	ND	ND
B	18.36	2.72	1.54	0.1836	0.0272	0.0154	ND	20	ND	ND	ND
Be	ND	ND	ND	ND	ND	N D	ND	ND	ND	ND	ND
Bi	2.10	0.072	0.216	0.021	0.0007	0.0022	ND	ND	ND	ND	ND
Cd	0.42	0.04	ND	0.0042	0.0004	ND	ND	ND	ND	ND	ND
Ca	1017	47	34	10.17	0.47	0.34	1000-1300	2500	0.78-1.02	0.04-0.05	0.026-0.034
Co	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Cr	0.18	ND	ND	0.0018	ND	ND	0.024-0.035	ND	5.14-7.5	ND	ND
Cu	6.66	2.69	1.67	0.0666	0.0269	0.0167	0.9	8.0	7.4	2.99	1.86
Fe	30.4	27.94	20.64	0.304	0.279	0.206	8-15	45.0	2.03-3.8	1.86-3.49	1.38-2.58
Mg	4386	312	240	43.86	3.12	2.40	310-320	350	13.71-14.14	0.98-1.01	0.75-0.77
Mn	808	3.90	4.05	8.08	0.039	0.0405	1.6-3.0	9.0	269.3-505	1.3-2.44	1.35-2.53
Mo	0.84	0.24	0.17	0.0084	0.0024	0.0017	0.045	2.00	18.67	5.33	3.78
Ni	7.14	0.65	0.77	0.0714	0.0065	0.0077	ND	1.0	ND	ND	ND
Pb	1.8	0.14	0.22	0.018	0.0014	0.0022	ND	ND	ND	ND	ND
Se	ND	ND	ND	ND	ND	ND	0.055	0.40	ND	ND	ND
Sr	32.16	2.57	2.24	0.3216	0.0257	0.0224	ND	ND	ND	ND	ND
V	1.68	0.144	0.024	0.0168	0.0014	0.0002	ND	ND	ND	ND	ND
Zn	24.24	8.59	8.32	0.2424	0.0859	0.0832	8-11	34.0	2.20-3.03	0.78-1.07	0.75-1.04

ND: Not Determined; CA= *C.afer*; NAS= Nigeria *A.sativum*; IAS = Indian *A.sativum* Source: FAO/WHO (Codex Alimentarius Commission). (2001); WHO (1998), Annette Dickinson. Council for Responsible Nutrition, 2002.

DISCUSSION

The elemental distribution in the fruit was compared to Dietary Reference Intakes (DRIs) (Table 5). If an average serving size of 10 g (dry mass) of CA or AS is consumed it would contribute significantly towards the daily intake of important nutrients. Most of the nutrients did not exceed their Tolerable Upper Intake Levels (TUILs) (Table 5). Manganese is one of the essential nutrients for nerve impulses and muscle contraction. About 10g of CA, NAS and IAS contributes about 269-500%, 1.3-2.4%, 1.4-2.5% respectively towards the RDA for Mn. Although the percentage contribution towards the RDA for Mn was high, the TUIL for Mn (9 mg per day) was not exceeded. If approximately 10 g of CA is consumed per day the contribution to the diet for the elements Cr would be <8% for CA whereas in AS and Fe, it was not detected. For the toxic elements, As, Pb and Cd, concentrations in both herbs were at safe levels for human consumption. In most part of Nigeria, especially in rural communities, many households rely on natural resources for food and CA and AS are frequently consumed by the people in most communities either as remedy or as a spice. This study provides information on the nutritive value of CA and AS which indicates that it is good for health considering the numerous essential elements it contain and does not have a tendency to accumulate toxic elements.

The elemental analysis revealed that the levels of Mg, Ca, Mn and Fe in *C. afer* leaf and *A.sativum* cloves were appreciably high compared to other minerals detected. These minerals are essential in the body system for disease prevention, control and may account for the ethnomedicinal effectiveness of *C. afer and A. sativum* in the treatment and management of several disease conditions. Calcium (Ca) is important for growth and maintenance of strong bones, muscular function, synthesis of enzymes, and normal physiological function of the body etc.[28] Magnesium serves as a cofactor for enzymes activation and biological structure promoter.[29]

Manganese is an important modulator of cells functions and play vital role in the control of diabetes mellitus.[30] Chromium has been shown to participate in sugar metabolism and possible in the prevention of diabetes.[31] Nickel serves as a cofactor of important antioxidant enzymes such as superoxide dismutase.[32] Copper is a very powerful pro-oxidant and catalyzes the oxidation of unsaturated fats and oils as well as ascorbic acid.[33] The level of Cd and Pb present in *C.afer* leaf was 0.42 and 1.80 respectively this level may not lead to any health hazard in consumers since it is lower than the maximum permissible limit of 30 mg/kg Pb for vegetables (Table 6)(FAO/WHO/2001)[28, 34] and thus are within safe limits for the use of *C. afer* leaf and *A.sativum* cloves as herbal medicine, this result did not agrees with that reported by Anyasor *et al*[10] in which the level of Pb was very low (0.01mg/kg) and Cd not detected in *C.afer* leave, this disparity in finding might result from the sample preparation, sensitivity of equipment as well as the environmental contamination as Rivers State is faced with the challenge of crude oil pollution. In the case of

Nigeria *A.sativum*, the level of Cd/Pb was 0.036/0.1444 mg/kg respectively while In India garlic Cd was not detected while the level of Pb was 0.216mg/kg which is in conformity with the report of Wodaje and Alemayehu[6] who reported present of lead and low level of Cd (0.10-0.16) in garlic cloves collected from different location in Ethiopia.

Table 6: Recommended Dietary Allowances (RDAs), Upper Level of intake (UL) (mg/day) of different elements for humans and maximum safe limit in plants (MSLP)(mg/kg).

ELEMENTS	MALE	FEMALE	UL(mg/day)	MSLP (mg/kg)
Arsenic (As)	NA	NA	NA	NA
Barium (Ba)	NA	NA	NA	NA
Boron (B)	NA	NA	20 c	NA
Beryllium (Be)	NA	NA	NA	NA
Bismuth (Bi)	NA	NA	NA	NA
Calcium (Ca)	1000 c	1000 c	2500 c	NA
Cadmium (Cd)	NA	NA	NA	0.3 b
Cobalt (Co)	NA	NA	NA	50 a
Chromium (Cr)	0.035 c	0.025 c	NA	23 a
Copper (Cu)	0.9 c	0.9 c	10 c	73 a
Iron (Fe)	8.0 c	18.0 c	45 c	425 a
Lead (Pb)	NA	NA	NA	30 b
Magnesium (Mg)	420 c	320 c	350 c	NA
Manganese (Mn)	2.3 c	1.8 c	11.0 c	500 a
Molybdenum (Mo)	0.045 c	0.045 c	2.0 c	NA
Nickel (Ni)	NA	NA	1.0 c	67 a
Selenium (Se)	0.055 c	0.055 c	0.4 c	NA
Silver (Ag)	NA	NA	NA	NA
Strotinum (Sr)	NA	NA	NA	NA
Zinc (Zn)	11 c	8 c	40 c	100 a

Source:[a]= FAO/WHO (Codex Alimentarius Commission). (2001), [b]= WHO (1998), [c]Annette Dickinson. Council for Responsible Nutrition, 2002, NA= not available, MSLP=maximum safe limit in plant, UL=upper limit.

Table 7: The upper intake levels (ULs) of elements for most individuals (Food and Nutrition Board, Institute of Medicine, National Academies, 2011).

Age	As (µg d^{-1})	Ca (mg d^{-1})	Cu (µg d^{-1})	Fe (mg d^{-1})	Mg (mg d^{-1})	Mn (mg d^{-1})	Ni (mg d^{-1})	Se (µg d^{-1})	Zn (mg d^{-1})	Cr (µg d^{-1})
15-50	ND	3000	8000	45	350	10	1	400	35	ND
50	ND	2500	10,000	45	350	11	1	400	40	ND

ND – Not determinable

Table 8: Dietary Reference Intake (DRIs): Recommended intakes for individuals (Food and nutrition Board, Institute of Medicine, National Academies, 2011).

Life stage group	Ca (mg/d)	Cr (µg/d)	Cu (µg/d)	Fe(mg/d)	Mg(mg/d)	Mn(mg/d)	Se (µg d^{-1})	Zn (mg d^{-1})
Children	800	15	440	10	130	1.5	ND	5.0
Adults	1000	35	900	8	420	1.9-2.2	55	11

ND – Not determinable

Calcium (Ca) is an important element that plays a major role in bones, teeth, muscular system and heart functions. Calcium is necessary for the coagulation of blood, the proper functioning of the heart and nervous system and the normal contraction of muscles.[35] Daily Ca intake lower than the recommended one could have serious negative effects for human health such as onset of osteoporosis, very common in menopausal women, hypertension, colon and breast cancer.[36-37] The result obtained from this study showed a Ca level of 1017.42±62.34mg/kg for CA which is below the maximum permissible limit for humans but the current result disagree with the report of Anyasor *et al*[10] who reported a Ca concentration of 7.49mg/kg for CA which is almost negligible compared with the present finding (1017.42 + 62.34mg/kg). For Nigeria/India garlic, the level of Ca detected was 47.196±8.24 and 34.932±3.40 respectively it does not also agree with Wodaje and Alemaheyu[6] and Divya et al[38] who reported higher concentration of 1209mg/kg and 355.61 for Ethiopia /India AS respectively, differences may be due to geographical location as well as environmental condition/contamination.

Magnesium deficiency is correlated with the impaired function of many enzymes utilizing high energy phosphate bonds, as in the case of glucose metabolism.[34] The recommended dietary intake of Mg is about 130mg per day for children, 310-320 mg per day for adult females and 400-420 mg per day for adult males as shown in table 7 and 8. Magnesium is important for human health because it regulates many physiological processes, such as bone growth, blood pressure, protein and nucleic acids metabolism, neuromuscular transmission and muscle contraction. Besides, Mg acts as a cofactor of many enzymes and has an important role in reducing asthma. Magnesium deficiency can increase the risk of osteoporosis, mainly in menopausal women, the risk of atherosclerosis and lead to oxidative stress.[39] From the present study Mg concentration of 4386.6±300.00mg/kg was reported for CA. The result of this study did not tally with the report of Anyasor *et al*[10] who reported Mg concentration of 4.01 for CA (insensitive equipment and analytical method used) also for the *A.sativum* the result agree with that reported by Wodage and Alemayehu[6] and that of Divya *et al*[37] who reported Mg concentration of 994 and 1046.15mg/kg for Ethiopia and India AS respectively as against 312.60±37.92 and 240.84±5.76mg/kg from the present finding for Nigeria/India garlic respectively. The difference noted in this result might come from the method of analysis and also from environmental influence. Though the maximum safe limit for plant (MSLP) was not detected for Mg (table 5), but the result obtained did not exceed the permissible limit or acceptable limit (table 4).

Zinc is essential to all organisms and has an important role in metabolism, growth, development and general well-being. It is an essential co-factor for a large number of enzymes in the body.[34] The present study reported Zn concentration of 24.24 ±0.96, 8.592±0.72 and 8.316±0.012 for CA, Nigeria /India AS respectively. The result did not differ from that reported by Wodaje and Alemayehu[6] and Divya *et al*[37] who reported a Zn concentration of 71.35 and 28.42 for AS respectively. The result obtained is within the Dietary Reference Intake (DRIs) both for children and adult (table 7 & 8) and also within the permissible and acceptable limit for Zn (table 5 & 6). The result is also below the maximum safe limit for plant (table 6) which implies that both CA and AS can serve as a good source of Zn for human consumption without exhibiting any toxicity.

The present study showed that the *C.afer* and *A.sativum* contain the same essential elements with non detection of Ag, As, Be, Co and Se in both *C.afer* and *A.sativum*. Selenium has an important role in thyroid hormone metabolism, as an essential component of the three deiodinase. Also the selenium deficiency has been reported to be correlated with thyroid dysfunctions.[40] From the result of the analysis Se was not detected both in CA and AS. It is obvious from above discussion that minerals both micro and macro play a vital role in variety of functions in human body and a proper balance has to be maintained for the well being. Lack, insufficient or excess intake of any of them can result to deleterious health effect. Other elements such as As, Cd, Hg and Pb, which are known as non-essential/toxic elements also accumulate in these plants[41-42] through environmental contamination. These non-essential/toxic metals are said to be non-biodegradable and bioaccumulates in the body to cause toxic effect with time. More importantly they exert diverse toxicological effects in animal and human systems. The present findings showed non-detection of As (*A.sativum*, *C.afer*), however, Cd (0.42 and 0.036mg/kg) were detected in CA and Nigeria AS respectively whereas Pb (1.80, 0.144 and 0.216mg/kg) was detected in CA and Nigeria/India AS respectively but it was below the permissible limit of 0.03 mg/100g and 1.0 mg/100g respectively, as prescribed by WHO.[43] Pb is a multi organ toxicant that affects virtually all the organs in the body. Screening of *C. afer* and *A. sativum* in this study indicates that it contain Cd and Pb but within the permissible limit, however, with increased use of Cd and Pb in everyday activities both industrial, agricultural and domestics, chances are abound of their contamination in earth crush with more of it been absorbed by the plant and thus increase the concentration since most of this toxic metals does not biodegrades instead it bioaccumulates in the environment and therefore continuous screening of the plants is required.

In conclusion, we are able to ascertain from the result obtained that there is no geographical or environmental contribution or influence in the composition of essential and heavy metal in the garlic as both the Nigeria and India *A.sativum* was found to contain same number of essential element with no significant difference in their concentration. Also the concentration or level of the essential element in both the *C.afer* and *A.sativum* in which the activity of most herbal products resides is within the permissible limit prescribed by WHO and so fit for human consumption and also can serve as a source of essential nutrient to man.

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