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BIOAVAILABILITY AND ENVIRONMENTAL IMPLICATIONS OF MAJOR AND TRACE METALS IN MANIHOT ESCULENTA (CASSAVA) GROWN ON SHALY AND CALCAREOUS SOILS IN PARTS OF SOUTHERN BENUE TROUGH, NIGERIA.

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ABSTRACT

The study was carried out to investigate the concentration of major and trace metals in shaly and calcareous soil and their uptake in cassava plant parts in order to compare the levels of this metals in both soils as well as the cassava plant growing on the soil. Soil samples (0-30 cm and 30-60 cm) depth and cassava plants (leaves, stems and tubers) were collected from cultivated farm lands and analyzed for major and trace metals. (Ca, K, Al, Na, Fe, Cu, Zn, Pb, Co and Mo) using inductively coupled plasma mass spectrometery (ICP-MS). The pH and L01 of the soil sample were also measured. Results show that calcareous soils were moderately acidic to basic while shaly soils were acidic to neutral. The organic matter content were relatively higher in surface soils than subsurface soils. Levels of metals were generally higher in shaly soils compared to calcareous soils except for Ca, Na, and Mo. Values of enrichment factors revealed deficiency to minimal enrichment (Ef<2) of Al, K, Ca, Fe and Na, moderate enrichment (Ef2-5) of Cu, Zn, and Co and significant enrichment (Ef5-20) of Mo and Pb for shaly soils. In the case of calcareous soils, minimal enrichment was noticed for Al, Fe, K, Cu and Ca while Na, Zn, Pb and Co showed moderate enrichment with only Mo indicated very high enrichment. The principal analysis for cancerous and shaly soils in the study area indicate that the main source of metals are environment, geochemical and anthropogenic activities.

KEYWORDS: Bioavailability, Environmental implications, major and trace elements, manihot esculental (Cassava) shaly and calcareous soil.

INTRODUCTION

Soil acts as a long-term sink of major and trace elements accumulation. The concentration of these metals in the natural soil depends on the geological substrate and the processes that form the soil (Alloway, 1990). The ability of soil-plant system to supply essential metals to a target plant or plant association during specific period depends on the release of these metals from solid to liquid phase, the movement of metals through the soil solution to plant roots and absorption of the metals by plants roots (Alloway, 1995).

In recent times, metals in soils and uptake by plants constitute a very important component of the environment hence emphasis is now directed on their impact (Ochelebe et al., 2020). Major and trace metals input to agricultural soils originate from various sources including atmospheric deposition, fertilizer and lime, biosolids, livestock manure, industrial by-products and compost. Natural sources from rocks also contribute significant amount of major and trace metals to soil (Weixuan et al., 2001). According to Alloway (1995) metals are released from the soil.

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The main sources of heavy metals to plants are their growth media (soil, water and air) from which this metals are taken up from their roots, leaves and stem of plants (Okereke et al., 2020). These sources of major and trace metals input can contribute meaningful levels of Ca, K, Al, Na, Fe, Cu, Zn, Pb, Co and Mo and among these Al, Pb, Cu, Co, Mo, Na and Zn are in the list of major metals of interest on bioavailability studies by the USA Environmental Protection Agency (EPA) (McKinney and Roger, 1992). Some of these metals such as such as Pb Co and Mo are potential health risk on humans.

Man absorbs these harmful elements through the food chain from the plant and animals; as plants absorb these elements from soil and animals in turn feed directly or indirectly on the plants for examples cassava peels and leaves are processed and used as animals fed (Samlafo et al., 2022). Cassava is a draught resistant crops and form a stable food for the teeming population of Nigeria. (Udiba et al., 2019) Recent study has shown that food contamination by human activities is alarming due to high food insecurity and the quest for survival, (Ogbonna et al., 2020). The subsequent uptake of what these metals and distribution in plants is therefore of critical importance in relation to man's health because man inject these metals from the plants and animals consumed (Udosen, 1997) Hence, the cycling of major and trace metals whether essential or non-essential in soil-plant system is important as it is also a pathway to man and animal affecting positively or adversely because the soil-plant system is an open system which allows these interaction (Turker, 1996).

METHODOLOGY

Location, Topography and Climate:

The study area lies between latitudes 05^{o} 03^{1}N and 06^{o} 15^{1}N and longitudes 08^{o} 14'E and $08^{o}45^{1}$E in Southern Benue Trough, Nigeria.

The area consist of plains which are welldrained by streams originating from the highly deformed fractured highlands. The streams generally show V-shaped valley patterns. The drainage pattern of the area is dendritic and flows southwards (Edet et al., 1998).

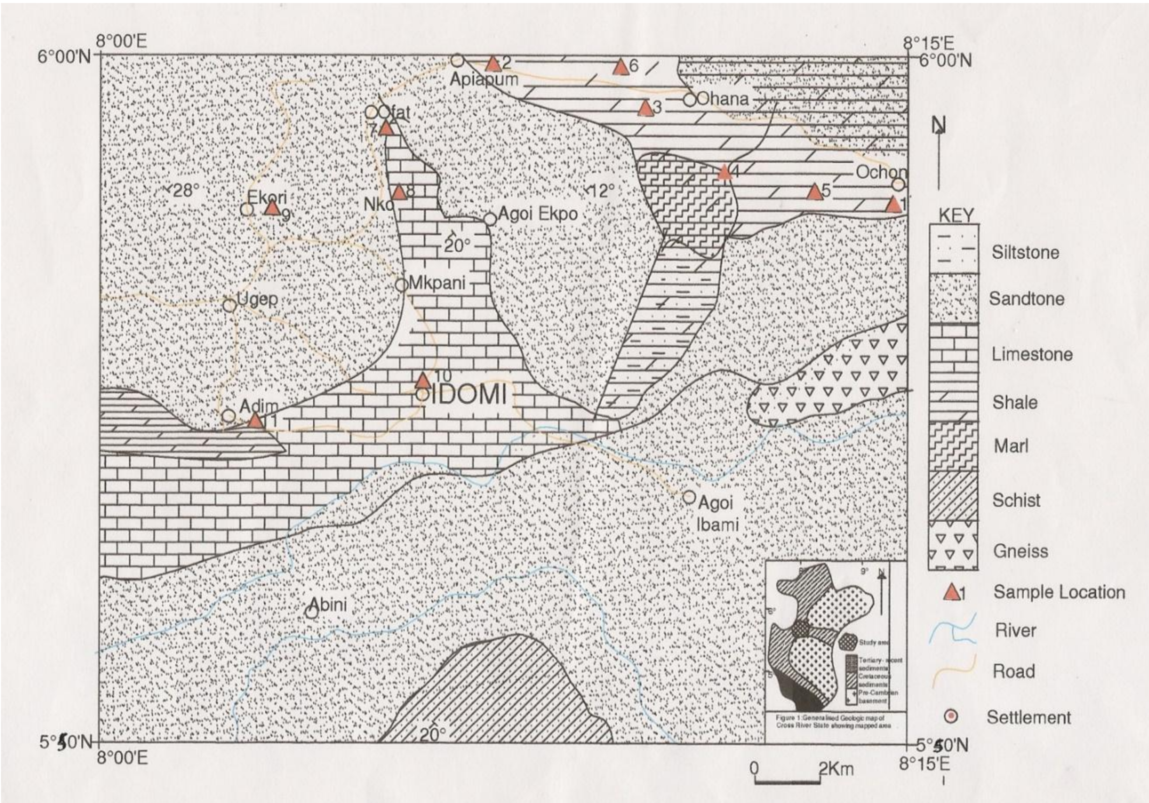


Figure 1: Geologic map of the study area showing sample locations

The climate of the study area is tropical humid characterized by two main seasons namely dry and wet seasons. The wet season starts from April to October with little break around the month of August usually called "August break". The dry season starts from November to March. The annual rainfall is between 200 and 250 cm (Illoeje, 2001). There is a period of harmattan characterized by dry, dusty and cool wind between the wet and dry seasons. The annual temperature ranges between 25ºC and 28ºC and generally high throughout the year (Ochelebe et al., 2017). During the wet season, the area is extremely humid with 78% humidity, which supports the luxuriant vegetation in the study area. The vegetation is tropical evergreen rainforest with unique combination of plants and animals.

Geology and mineralization

The study area is underlain by Cretaceous sediments and associated intrusive of south eastern Nigeria (Fig 1.) The Cretaceous sediments consist of AsuRiver Group and EzeAku Group. AsuRiver Group is the basal and oldest recorded sedimentary unit in the study area. It is dominated by bluish grey/black to olivine brown shale and sandy shale, fine grained micaceous calcareous sand stone and siltstone with limestone lenses (Petters et al., 1987). The EzeAku Group flanks the Asu-River Group (Offodie, 1992). The EzeAku Formation consist of the late Cenomanian Ezilo Shale Member which comprises mostly dark gray shale with fine sand stone and silt stone intercation and the late Turonian Amaseri Sandstone Member consisting of basal and fossiliferous shales and highly bioturbated sand stone (Petters et al., 1987).

Field study

Plant and soil samples were collected from different locations overlain by shaly and the cancerous terranes (Fig 1.).

About 2g representative core soil samples were collected at depth of 0-30cm and 30-60cm from each sampling point using a hand auger from cultivated farm lands around the study area. At the same time, cassava plant samples were collected on the plot where soil samples were taken. Cassava was chosen because its dominance in the area, and it is a major source of food for the people. Different parts of cassava plants were collected to properly asses uptake and transfer of major and trace metals from the soil.

Laboratory study

The soil sample were air dried at room temperature (approximately 30ºC) disaggregated and sieved with 0.5 mm mesh size. The samples were packed in polythene sachets and labelled for digestion.

The plant samples were air-dried in the samples bags at moderate temperature to reduce the level of moisture content. The cassava tubers were pilled, washed with distilled water and oven dried at 100ºC. The dried plant samples were milled using porcelain mortar and pestle, packaged in polythene sachets and label for digestion.

0.5g of powered samples of both soil and plants were weighed into 100ml glass beakers. The samples were then moistened with few drops of distilled water and 10ml of concentrated $4MHNO_3$ added into each backer. The backers were then covered with glass disc and placed into fumed chamber on a sand bath over a hot plate. The mixture were refluxed at moderate temperature to dryness forming a white cake mineral. The mineral residue was leached with 5ml of HCl into already calibrated labelled test tube and made up to 10ml with distilled water. The test tubes were sealed with plastic stoppers and taken for analysis for some major and trace metals (Ca, K, Al, Na, Fe, Cu, Zn, Pb, Co and Mo) using inductively coupled plasma mass spectrometer (ICP-MS) model 6000/9000 Perkin Elemer Etan instrument with detection limits of about several Pg/g in solutions corresponding to a determination limit of about 100 ppb in solid samples. 0.5gm of powered plant samples were weighed into glass beakers and moisture with distilled water 20ml of $4MHNO_2$ and $HClO_4$ in the ration of 3:1 was added into each beaker. The beakers were then covered with glass disc and placed into a fume chamber on a sand over a hot plate. The mixtures were refluxed at moderate temperature for one hour and heated for four hours forming a white cake mineral. The mineral residue were leached with 5ml of HCl and filtered with 110mm paper into well labeled and calibrated text tubes and made up to 10ml with distilled water. The test tubes were sealed with plastic stoppers and taken for analysis. Both soil and plants samples were digested and analysed at the ACME Laboratory Vancover, Canada.

A quality control programme such as regent blanks, replicate and duplicate samples were used to access the accuracy and precision of the chemical data for soils and plants.

RESULTS AND DISCUSSION

Physical parameters in soils: The summary statistics of the physical parameter and elemental composition of the soils of the study area at 0 – 30 cm and 30 -60 cm depth are presented in Tables 1-4.

Table 1: Summary statistics of physical properties and metal levels in surface soil (0-30 cm depth) of the shaly area.

	PH	OM %	Ca %	K %	AL %	Na %	Fe %	Cu mg/kg	Zn mg/kg	Pb mg/kg	Co mg/kg	Mo mg/kg
CV%	9.12	16.74	43.45	23.83	11.54	38.55	36.09	15.91	37.00	43.40	30.13	51.63
Mean	5.70	6.69	1.45	2.56	6.93	0.86	5.07	91.90	322.00	145.90	69.40	22.70
STD	0.52	1.12	0.63	0.61	0.80	0.32	1.83	14.62	119.16	63.32	20.91	11.72
Min	4.80	3.90	0.60	1.66	5.20	0.47	1.80	69.00	196.00	74.00	36.00	8.00
Max	6.60	7.80	2.26	3.56	8.20	1.47	7.00	116.00	562.00	250.00	96.00	48.00
WHO (2016)							50,000	100	300	100	50	NA

Na – Not available, WHO- World Health Organization

Table 2: Summary statistics of physical properties and metal levels in surface soil (0-30cm depth) of the (calcareous) area.

	pH	OM %	Ca %	K %	Al %	Na %	Fe %	Cu mg/kg	Zn mg/kg	Pb mg/kg	Co mg/kg	Mo mg/kg
CV%	7.93	60.54	11.00	25.90	33.18	42.03	42.41	39.46	42.97	46.67	16.66	28.34
Mean	6.56	4.08	2.00	1.66	4.40	1.38	2.90	72.80	25.80	59.20	92.40	56.80
STD	0.52	2.47	0.22	0.43	1.46	0.58	1.23	28.73	54.05	27.63	15.39	16.10
Min	5.80	1.60	1.64	1.20	2.68	0.96	1.00	33.00	192.00	24.00	76.00	40.00
Max	7.20	7.00	2.20	2.20	6.32	2.40	4.30	112.00	306.00	96.00	112.00	80.00
WHO (2016)							50,000	100	300	100	50	NA

Na – Not available, WHO- World Health Organization

Table 3: Summary statistics of physical properties and metal levels in sub-surface soil (30-60cm depth) of the shaly area.

	pH	OM %	Ca %	K %	Al %	Na %	Fe %	Cu mg/kg	Zn mg/kg	Pb mg/kg	Co mg/kg	Mo mg/kg
CV%	9.84	25.09	42.17	29.34	16.88	29.29	46.13	31.99	21.38	67.96	28.70	65.48
Mean	6.30	5.42	1.66	2.59	6.28	0.99	5.42	144	382.80	206.40	110.80	25.00
STD	0.62	1.36	0.70	0.76	1.06	0.29	2.50	46.07	81.85	140.27	31.57	16.37
Min	5.60	3.20	0.84	1.60	4.80	0.66	2.20	84.00	276.00	48.00	69.00	6.00
Max	7.20	6.70	2.50	3.40	7.30	1.40	8.20	201.00	492.00	366.00	144.00	51.00
WHO (2016)							50,000	100	300	100	50	NA

Na – Not available, WHO- World Health Organization

Table 4: Summary statistics of physical properties and metal levels in sub-surface soil (30-60cm depth) of the calcareous area.

	pH	OM %	Ca %	K %	Al %	Na %	Fe %	Cu mg/kg	Zn mg/kg	Pb mg/kg	Co mg/kg	Mo mg/kg
CV%	6.09	23.01	25.57	36.36	48.04	32.35	15.55	56.80	22.25	28.90	46.34	34.67
Mean	7.38	2.52	3.52	1.10	2.04	2.04	1.80	47.00	159.20	33.00	47.60	78.40
STD	0.45	0.58	0.90	0.40	0.98	0.66	0.28	26.70	35.42	9.54	22.06	27.18
Min	6.80	1.80	2.00	0.60	1.26	0.90	1.40	22.00	111.00	22.00	26.00	50.00
Max	8.00	3.00	4.20	1.70	3.60	2.60	2.00	92.00	202.00	45.00	80.00	112.00
WHO (2016)							50,000	100	300	100	50	NA

Na – Not available, WHO- World Health Organization

Variations of soil composition and metal concentration with lithology and depth

Calcareous soils were moderately, acidic to basic with pH values ranging from 5.8 – 7.2 and 6.8 – 8.0 in the surface and subsurface soils respectively. This pH could attributed to the decomposition of organic matter content in soil, a process which is often rapid in tropical environment such as the study area. The basic nature of the soil could be attributed to the dissolution of calcium carbonate associated with calcareous regions by rain water. The organic matter content of the surface soil (0-30 cm) depth was high (1.6-70%) compared to the subsurface (30-60 cm) depth (1.8 -3.0%) indicating high decomposition of dead organisms and materials on the surface area.

Shaly soil were acidic to neutral with pH value ranging from 4.8 – 6.6 and 5.6 – 7.2 in surface and subsurface soils respectively. Apart from decomposition of organic matter which may enhance the nature of the soil, the acidic nature of the soils could be attributed to acidic oxides associated with geochemical weathering of shales (Jingzh et al., 2012). The organic contents of the surface soil of the area (0 – 30cm depth) was high (3.9-7.9%) compared to subsurface soil (30-60cm depth) with values ranging from (3.2 – 6.7%).

Generally, the surface calcareous and shaly soils in the study area were high in organic matter content, an indication of high degree of decomposition of dead materials from plants and animals.

Metals concentration for both shaly and calcareous soils shows wide range of values and variability of metal concentrations of soils in the area. This variation could be attributed to different rock type found in the area mainly shales and limestone. Environment and human input could also play a vital role in the variability of metals. Studies by Briggs et al., (1997) agree that spatial variability of metal content in soil is subject to lithology, environmental control and human input. A closer observation of figures 2-5 reveals that metals concentration were higher in shaly soils, except for Ca, Na and Mo, relative to calcareous soils. These concentration of soils tends to reflect their geochemical composition from their parent rock (Weixuan et al., 2001).

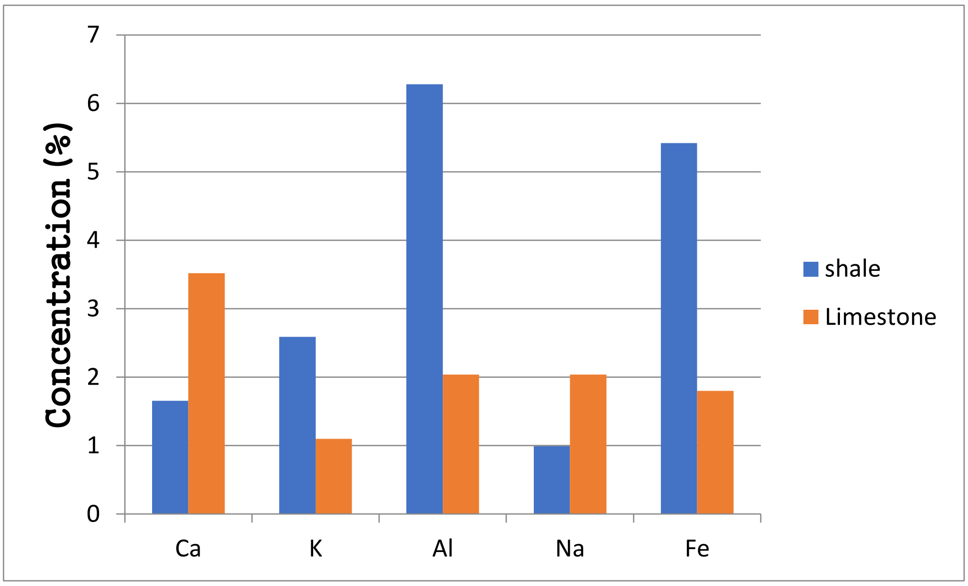


FIG. 2: Comparison of metal levels in soils over shaly and calcareous area at depth (0-30cm).

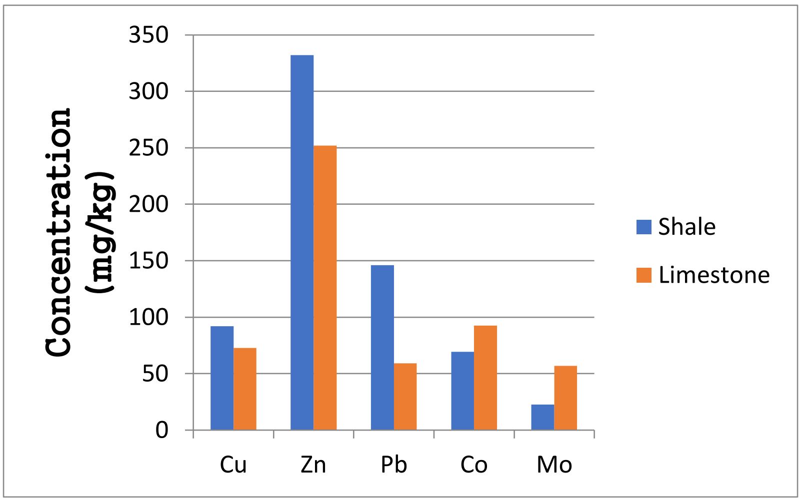


FIG. 3: Comparison of results of metal levels in soils over shaly and calcareous area at depth (0-30cm).

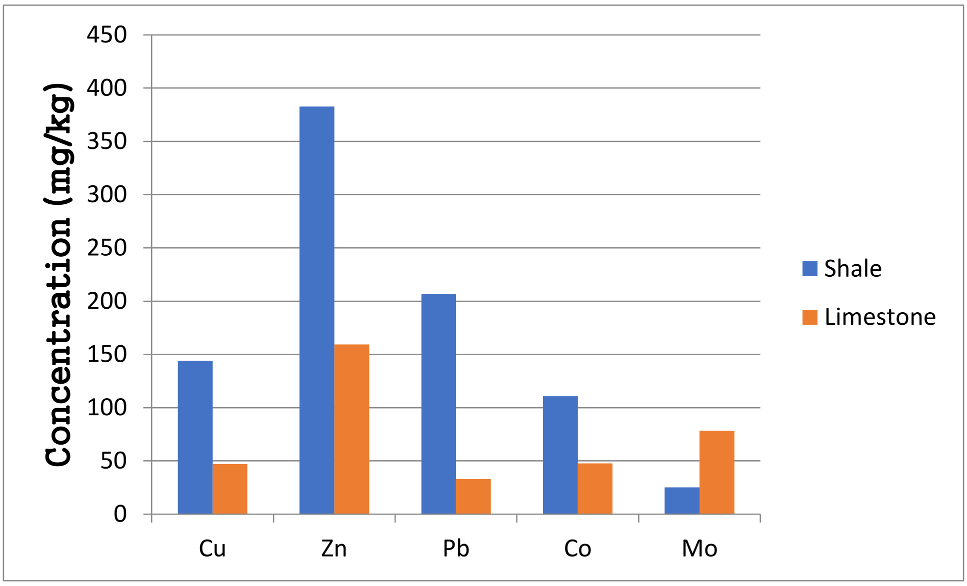


FIG. 4: Comparison of metal levels in soils over shaly and calcareous areas at depth (30-60 cm).

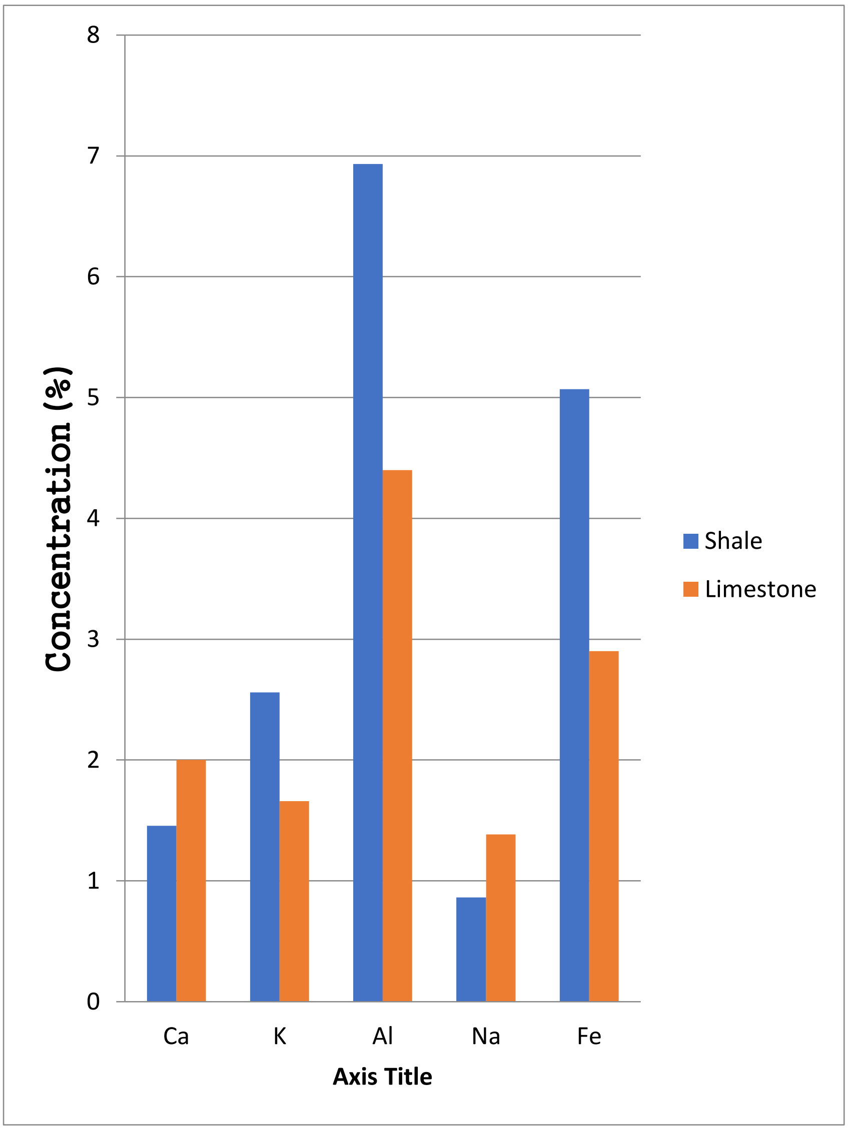


FIG. 5: Comparison of results of metal levels in soils over shaly and calcareous areas at depth (30-60 cm).

Concentration of metals in parts of cassava plant: The summary statistics of elemental composition of Manihot esculenta (Cassava) in the study area is presented in Tables 5 & 6.

Table 5: Summary statistics of elemental composition of cassava parts in the shaly area

Leaves

	Ca %	K %	Al %	Na %	Fe %	Cu mg/kg	Zn mg/kg	Pb mg/kg	Co mg/kg	Mo mg/kg
Mean	0.08	0.19	0.02	0.02	0.01	10.08	111.70	2.68	0.87	1.23
STD	0.04	0.08	0.03	0.01	0.00	1.57	26.92	2.01	0.55	2.11
Min	0.02	0.02	0.00	0.01	0.00	1.58	26.92	1.00	0.28	0.00
Max	0.13	0.31	0.01	0.05	0.02	11.60	154.00	7.31	1.85	6.18

Stems

	Ca %	K %	AL %	Na %	Fe %	Cu mg/kg	Zn mg/kg	Pb mg/kg	Co mg/kg	Mo mg/kg
Mean	0.12	0.29	0.12	0.04	0.01	5.74	12.48	1.64	0.89	0.06
STD	0.06	0.26	0.04	0.03	0.00	3.93	1.99	1.07	0.18	0.08
Min	0.06	0.02	0.08	0.02	0.00	2.20	11.20	0.60	0.66	0.01
Max	0.21	0.60	0.18	0.10	0.01	12.20	16.00	3.12	1.12	0.20

Tubers

	Ca %	K %	AL %	Na %	Fe %	Cu mg/kg	Zn mg/kg	Pb mg/kg	Co mg/kg	Mo mg/kg
Mean	0.15	0.16	0.03	0.14	0.01	2.43	10.82	0.62	0.98	2.26
STD	0.23	0.22	0.02	0.08	0.01	0.84	3.02	0.82	0.72	3.10
Min	0.01	0.04	0.01	0.01	0.00	1.24	6.49	0.00	0.01	0.06
Max	0.80	0.78	0.07	0.24	0.03	4.09	16.33	2.48	2.01	10.2

Table 6: Summary statistics of elemental composition of cassava parts in the calcareous area

Leaves

	Ca %	K %	AL %	Na %	Fe %	Cu mg/kg	Zn mg/kg	Pb mg/kg	Co mg/kg	Mo mg/kg
Mean	0.18	0.56	1.16	1.95	0.01	5.80	115.20	1.24	0.72	0.01
STD	0.13	0.19	0.55	0.70	0.01	1.96	54.09	0.24	0.41	0.01
Min	0.08	0.36	0.60	1.00	0.01	3.60	74.00	1.01	0.20	0.01
Max	0.40	0.82	2.00	2.62	0.02	8.20	208.00	1.60	1.20	0.03

Stem

	Ca %	K %	AL %	Na %	Fe %	Cu mg/kg	Zn mg/kg	Pb mg/kg	Co mg/kg	Mo mg/kg
Mean	0.22	0.34	0.08	0.02	0.01	8.80	8.96	0.72	0.80	0.24
STD	0.05	0.29	0.05	0.01	0.01	4.15	2.40	0.80	0.32	0.11
Min	0.18	0.04	0.02	0.01	0.00	4.00	6.60	0.16	0.40	0.10
Max	0.30	0.80	0.14	0.04	0.03	14.00	12.00	2.00	1.20	0.40

Tubers

	Ca %	K %	AL %	Na %	Fe %	Cu mg/kg	Zn mg/kg	Pb mg/kg	Co mg/kg	Mo mg/kg
Mean	0.24	0.52	0.18	0.04	0.01	1.16	5.30	0.01	0.32	1.32
STD	0.31	0.49	0.01	0.02	0.01	0.43	2.34	0.01	0.13	0.48
Min	0.01	0.10	0.01	0.02	0.01	0.43	2.16	0.00	0.13	0.48
Max	0.80	1.12	0.04	0.06	0.02	1.60	8.54	0.02	0.50	0.20

Bioaccumulation: This is also known as accumulation factor or concentration factor and used to estimate the uptake ratio of plants from soils. This is to establish the relationship between metal concentration in soil and its uptake by plants. It is define as metal concentration in plant divided by total metal concentration in soil (Jackson et al.. 1991; Sutherland, 2000). It shows the relationship between the level of metals present in soils and plants in the area. Plants take up metals in either ionic or complex forms (Sharma et al., 2007, Jung, 2008).

BA=$\frac{(\text{C plant})}{(\text{C soil})}$ where C plant is metals concentration in plant and C soil is metals in soil.

Accumulation factor was determined for all the parts of plant and other ratios such as leaves/tubers, leaves/stems, stems/tubers were calculated and presented in table 7 and 8, Sharmal et al., (2007), Jung (2008) indicated that bioavailability of metals in plant tissue depend upon factors such as pH, soil moisture, organic matter and metals availability and the presence of complexing elements such as Ca, Na and K affect the bioavailability of trace elements in soil. The physiological response of plant does not exert control on the degree of uptake and bioaccumulation of different metals (Kabata – Pendias, 2004). Generally there were variability in the metal concentration of plant parts in the study area for both calcareous and shaly soils (table 7 and 8). The variation in elemental contents in plant parts could be attributed to the complex interactions among numerous factors that influenced the availability of metals. The solubility and hence availability of metals depended on one or a combination of soil properties, including pH, Cation Exchange Capacity (CEC), organic matter, clay content, Eh, salinity, presence of other metals among others (Kerner and Wollman, 1992). The variation in phyto availability of metal and uptake factor for these metals may also be attributed to the fact that the respective total metals content does not represent the bioavailable fractions for plants uptake (Mc-Bride et al., 1997, Ma and Rao, 1997). This could also be attributed to the environmental conditions of the area especially pH which influence the degree competitive absorption between two similar charged metal species (Harter, 1992).

TABLE 7: Accumulation factor/other ratios of plant parts in the calcareous area

S/No	Metal	Mean reading of soil (0-30 cm)	Mean reading of cassava plant parts			Calculated plant parts uptake ratio			Other ratios		
			Leaves	Stems	Tubers	Leaves	Stems	Tubers	L/S	L/T	S/T
1	Ca	2.79	0.18	0.22	0.24	0.06	0.07	0.09	0.82	0.75	0.92
2	K	1.38	0.56	0.34	0.52	0.41	0.25	0.38	1.65	1.07	0.65
3	Al	3.21	1.16	0.08	0.02	0.36	0.03	0.02	14.50	58.00	4.00
4	Na	1.71	1.95	0.02	0.04	1.14	0.01	0.02	97.50	48.75	0.50
5	Fe	2.35	0.01	0.015	0.01	0.004	0.01	0.004	0.67	1.00	1.50
6	Cu	59.90	5.80	8.80	1.16	0.10	0.15	0.02	0.66	5.00	7.59
7	Zn	205.50	115.20	8.96	5.30	0.56	0.04	0.03	12.86	21.74	1.69
8	Pb	46.10	1.24	0.72	0.008	0.03	0.02	0.00	1.72	155.00	90.00
9	Co	70.00	0.72	0.8	0.32	0.01	0.01	0.005	0.90	2.25	2.50
10	Mo	67.60	0.02	0.24	1.32	0.00	0.004	0.02	0.08	0.02	0.18

L-Leaves, S-Stems, T-Tubers

TABLE 8: Accumulation factor/other ratios of plant parts in the shaly area

S/No	Metals	Mean reading of soil (0-30 cm)	Mean reading of cassava plant parts.			Calculated plant parts uptake ratio			Other ratios		
			Leaves	Stems	Tubers	Leaves	Stems	Tubers	L/S	L/T	S/T
1	Ca	1.57	0.087	0.12	0.15	0.06	0.08	0.10	0.73	0.58	0.80
2	K	2.58	0.21	0.29	0.16	0.08	0.11	0.06	0.72	1.31	1.81
3	Al	6.60	0.091	0.12	0.03	0.003	0.02	0.005	0.75	3.03	4.00
4	Na	0.93	0.02	0.04	0.14	0.02	0.04	0.15	0.50	0.14	0.28
5	Fe	5.25	0.006	0.005	0.012	0.001	0.001	0.002	1.20	0.50	0.42
6	Cu	117.95	10.08	5.74	2.43	0.09	0.05	0.02	1.75	4.15	3.36
7	Zn	357.4	111.72	12.48	10.82	0.31	0.03	0.03	8.95	10.33	1.15
8	Pb	176.15	2.77	1.64	0.62	0.02	0.01	0.00	1.69	1.64	2.65
9	Co	90.10	0.87	0.89	1.04	0.01	0.01	0.01	0.98	0.84	0.86
10	Mo	19.54	1.23	0.06	2.26	0.06	0.00	0.12	20.5	0.54	0.02

L-Leaves, S-Stems, T-Tubers

Different plant parts contain different quantity of metals, figs 6-9. The concentration of K for all plant parts is high, an indication that K is required by all parts of the plant even though there still variation. Generally, the concentration of metals in plant parts for most elements such as K, Ca, Al, Cu, Zn and Na were high in leaves and stems except for Ca/Na in the shaly soils and Ca/K in the calcareous soils where concentration was high in tubers. Elemental accumulation in leaves is not always correlated with toxicity especially in the case of the metal necessary to plant metabolism (essential metals).

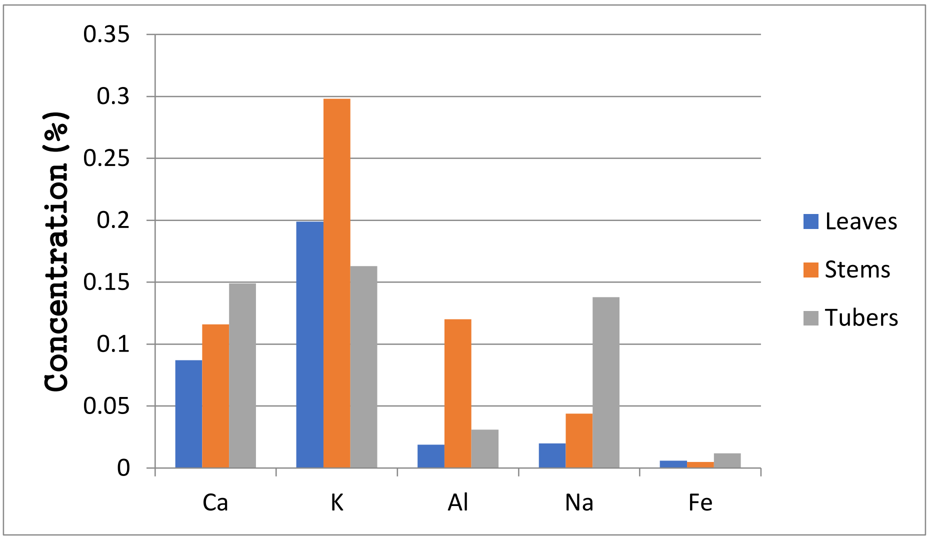


FIG. 6: Bar charts showing mean levels of elements in leaves, stems and tubers from the shale area.

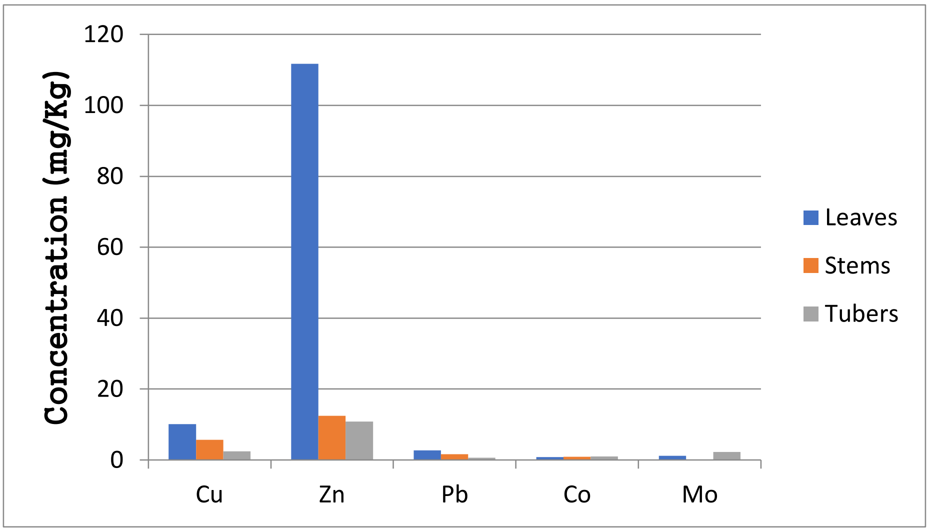


FIG. 7: Bar charts showing mean levels of elements in leaves, stems and tubers from the shale area.

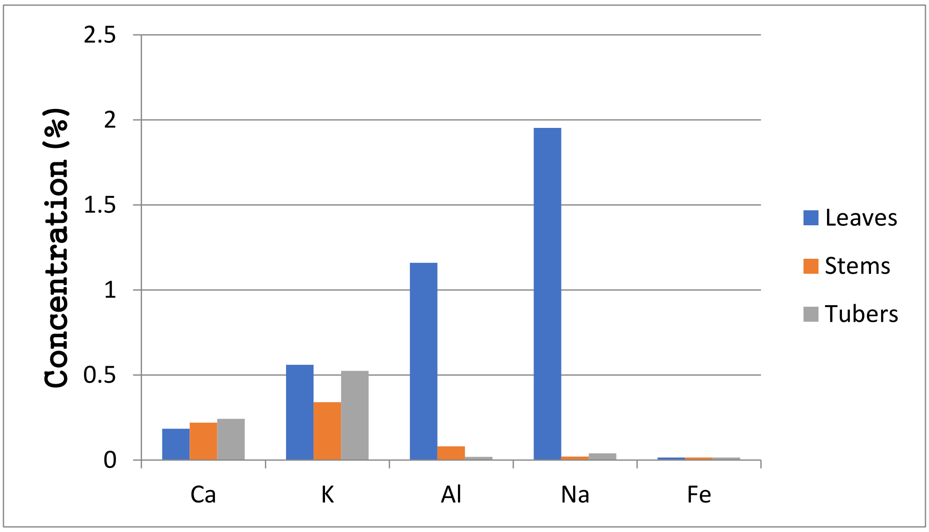


FIG. 8: Bar charts showing mean levels of elements in leaves, stems and tubers from the limestone area.

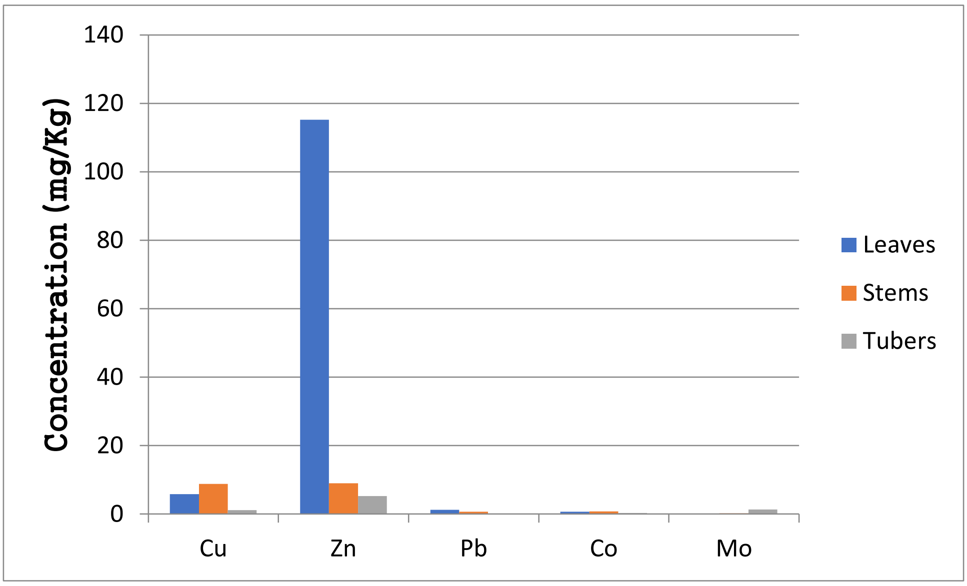
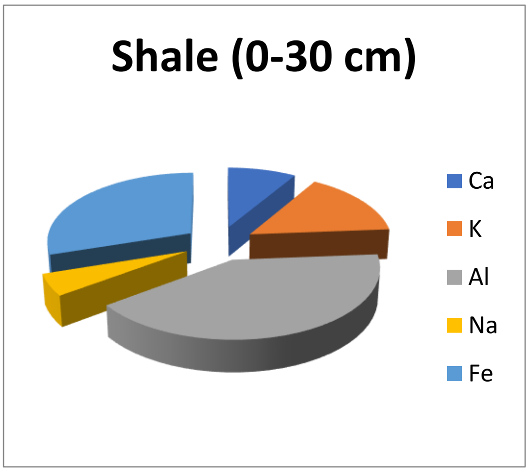


FIG. 9: Bar charts showing mean levels of elements in leaves, stems and tubers from the limestone area.

The high concentration of these metals in the tubers indicates the degree of metals accumulation in the soils and offers clues on the soil metals content (Ana-Irina et al., 2008. This relationship is further simplified in figs 10-13 where the different metals for both soils are taken up by plants based on the concentration in soils and the metal requirement of the plant part (Farogo and Merha, 1991).

The concentration of these metals in different parts (leaves, stems and tubers) from both shaly and calcareous soils as computed from the other ratios of the plant leaves/stems, leaves/tubers and stems/tubers (table, 7/8) is an indication of transfer mechanisms and bioaccumulation behavior of these metals between plant parts. However, it is worthy to note that, local, seasonal and temporal variations can reduce alterations in soil and plant parts composition. Some important factors to take into account are, the leaching of soils, the age and solar exposure of plant (Alvarenga et al., 2003).



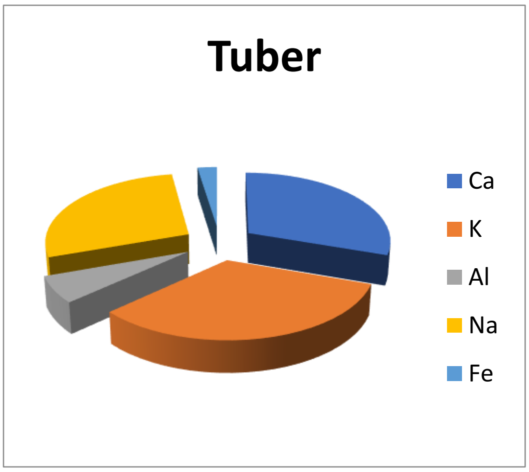


FIG. 10: Pie charts showing relative composition of elements in soil (shale) and tubers.

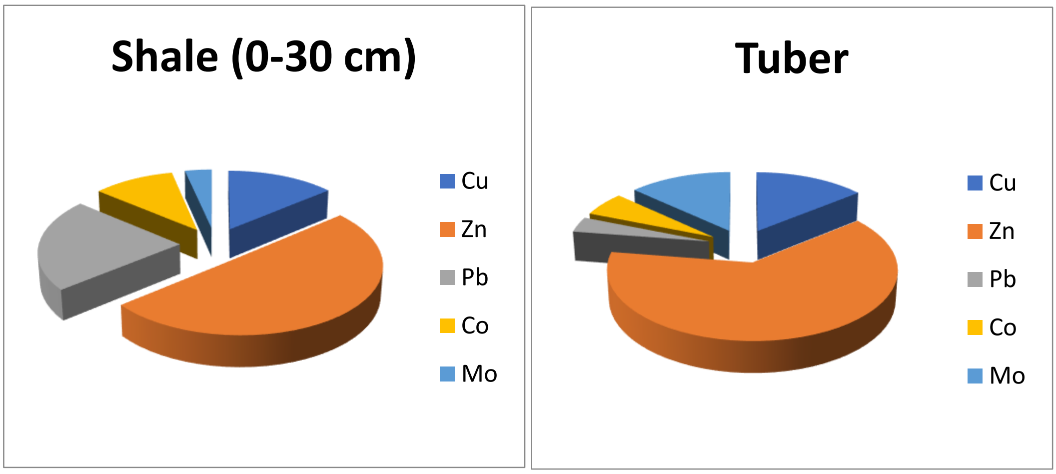


FIG. 11: Pie charts showing relative composition of elements in soil (shale) and tubers.

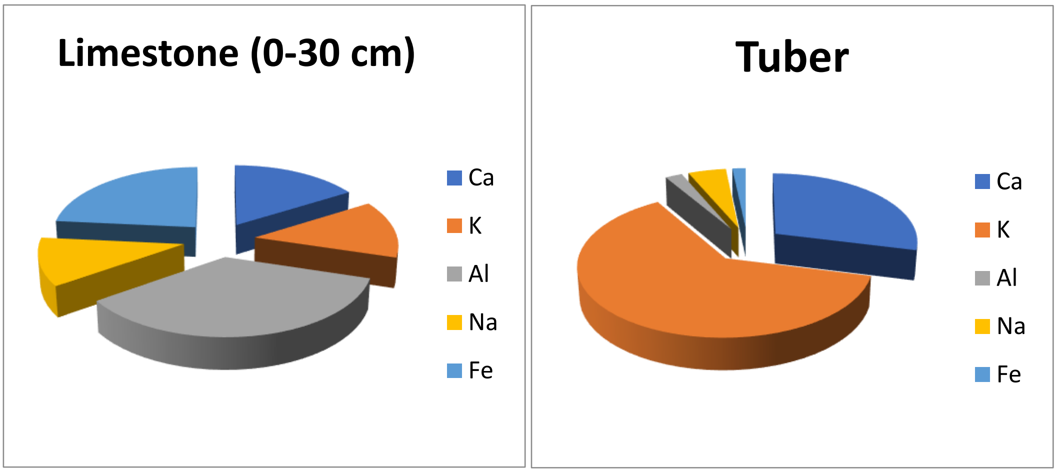


FIG. 12: Pie charts showing relative composition of elements in soils (limestone) and tubers.

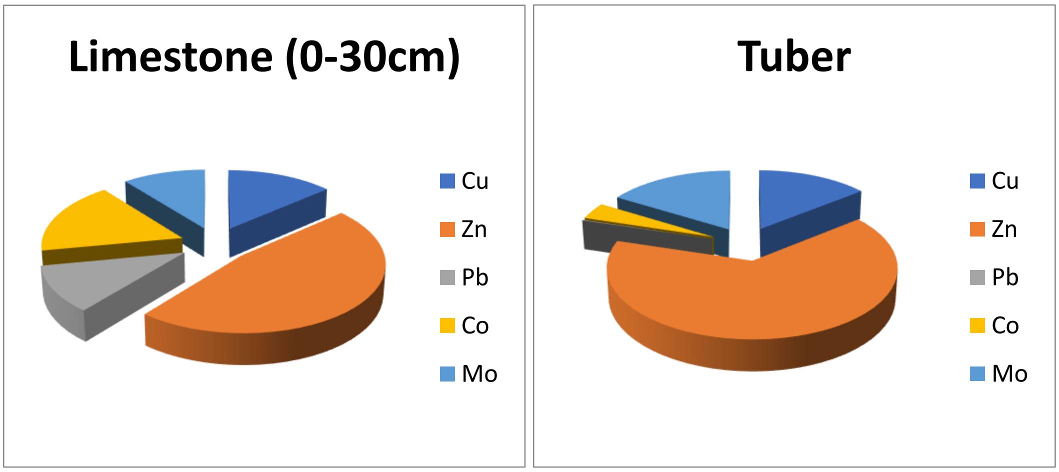


FIG. 13: Pie charts showing relative composition of soils (limestone) and tubers.

Correlation analysis: To determine common inter-correlation between constituent metals and also to aid in the interpretation of geochemical data, correlation analysis was carried out. According to Ntekim et al., (1992) most geochemical data and a number of metals display similar patterns of distribution because these metals are controlled by similar processes. Tables 9-12 presents the result of correlation analysis of soils at different depth from the study area. The result for soil from calcareous area at depth (0 – 30cm) table 9 showed high positive correlation between Al and Mo (r = 0.96) at level p< 0.01 while Al and OM (r=-0.92), Pb and K (r = -0.89) and Fe and Na (r= 0-0.94) showed negative correlation at level P<0.05. At calcareous area (30 – 60cm) depth, table 10, only Mo and Zn showed high negative correlation (r = -0.96) and the correlation is significant at P<0.01 level. The result for soils at depth (0-30cm) table 11 of the shaly area showed significant positive correlation (p<0.01) between Cu and Fe (r=0.79) and Co and Fe (r=0.78). At depth (30-60cm) shaly area table 12, only Cu and Om (r=0.90) show significant positive correlation (P<0.05) while high negative correlation (P<0.05) where observed between Al and Ca (r= -0.89), Cu and Ca (r = 0.89) and between Na and K (r = -0.93)

TABLE 9: Correlation analysis of calcareous area 0-30 cm depth

	pH	OM	Ca	K	Al	Na	Fe	Cu	Zn	Pb	Co	Mo
pH	1											
OM	0.46	1										
Ca	-0.20	-0.399	1									
K	0.18	0.2	-0.145	1								
Al	-0.45	-.921*	0.441	0.179	1							
Na	-0.78	-0.091	0.389	-0.514	-0.019	1						
Fe	0.69	-0.023	-0.542	0.278	0.019	-.942*	1					
Cu	0.70	0.627	-0.243	-0.447	-0.828	-0.176	0.229	1				
Zn	-0.54	0.004	-0.156	0.707	0.292	0.129	-0.244	-0.766	1			
Pb	-0.059	-0.319	-0.16	-.898*	-0.073	0.188	0.117	0.403	-0.695	1		
Co	0.228	-0.643	-0.088	0.267	0.672	-0.698	0.751	-0.345	-0.046	0.09	1	
Mo	-0.307	-0.863	0.62	0.199	.966**	-0.048	-0.015	-0.741	0.189	-0.16	0.628	1

* Correlation is significant at the 0.05 level (2-tailed)
** Correlation is significant at the 0.01 level (2-tailed)

TABLE 10: Correlation analysis for calcareous area 30-60 cm depth

	pH	OM	Ca	K	Al	Na	Fe	Cu	Zn	Pb	Co	Mo
pH	1											
OM	-0.587	1										
Ca	-0.672	0.871	1									
K	-0.17	0.641	0.827	1								
Al	-0.219	-0.276	0.122	0.045	1							
Na	-0.483	0.002	-0.196	-0.703	0.093	1						
Fe	-0.275	0.368	0.706	0.745	0.674	-0.367	1					
Cu	0.14	0.214	0.378	0.725	-0.3	-0.878	0.218	1				
Zn	0.123	0.072	0.087	0.333	-0.6	-0.601	-0.279	0.862	1			
Pb	-0.076	0.173	0.587	0.819	0.522	-0.71	0.871	0.611	0.164	1		
Co	0.841	-0.389	-0.621	-0.204	-0.681	-0.417	-0.625	0.312	0.505	-0.33	1	
Mo	0.111	-0.259	-0.239	-0.349	0.632	0.444	0.273	-0.798	-.967**	-0.102	-0.342	1

** Correlation is significant at the 0.01 level (2-tailed).

TABLE 11: Correlation analysis for shaly area 0-30 cm depth

	pH	OM	Ca	K	Al	Na	Fe	Cu	Zn	Pb	Co	Mo
pH	1											
OM	0.291	1										
Ca	0.081	-0.503	1									
K	0.051	0.461	-0.447	1								
Al	0.317	-0.066	0.114	-0.493	1							
Na	0.495	0.151	-0.177	-0.488	0.558	1						
Fe	-0.398	0.025	-0.035	0.037	-0.42	-0.356	1					
Cu	-0.559	-0.04	-0.033	-0.212	-0.139	-0.175	.799**	1				
Zn	0.006	0.237	0.202	-0.406	0.301	0.112	-0.338	-0.021	1			
Pb	0.404	0.267	0.162	-0.032	-0.27	0.09	-0.42	-0.44	0.586	1		
Co	-0.425	0.399	-0.263	0.472	-0.62	-0.631	.785**	0.608	-0.099	-0.124	1	
Mo	0.107	0.184	-0.413	0.446	0.384	0.077	-0.51	-0.286	-0.181	-0.328	-0.261	1

** Correlation is significant at the 0.01 level (2-tailed)

TABLE 12: Correlation analysis of shaly area 30-60cm depth

	pH	OM	Ca	K	Al	Na	Fe	Cu	Zn	Pb	Co	Mo
pH	1											
OM	-0.555	1										
Ca	0.111	-0.868	1									
K	-0.102	0.6	-0.549	1								
Al	0.197	0.613	-.898*	0.219	1							
Na	-0.045	-0.314	0.307	-.932*	0.008	1						
Fe	0.44	0.384	-0.58	0.716	0.547	-0.586	1					
Cu	-0.33	.900*	-.890*	0.333	0.818	0.006	0.433	1				
Zn	-0.67	0.124	0.181	-0.596	-0.149	0.759	-0.656	0.226	1			
Pb	-0.604	0.208	-0.073	-0.162	-0.088	0.098	-0.692	0.004	0.351	1		
Co	0.517	-0.702	0.391	-0.686	-0.084	0.444	-0.481	-0.546	-0.091	0.261	1	
Mo	-0.648	-0.19	0.648	-0.142	-0.861	0.073	-0.602	-0.425	0.506	0.268	-0.257	1

- Correlation is significant at the 0.005 level (2-tailed)

Principal Component analysis (PCA): PCA helps to reduce the complex nature of an inter-correlation data. The results gives greater efficiency in terms of information comparison over the original data and ability to interpret (Vousta et al., 1996). The result of the Principal Component Analysis (PCA) for soils at depth 0-30 cm is present in tables 13 and 14.

PCA aided and strengthened the interpretation and identification of the source and control of metals distribution in the area. For the calcareous soils three principal components explaining about 88% of the information contained in the original data set while in the shaly soils about 91% data variability explained by a five component situation. The first to third components of the calcareous soils and the first to fourth components of the shaly soils relates environment, geochemical and anthropogenic controls. Anthropogenic controls include agricultural practices such as application of fertilizer, pesticides and herbicides which contribute to nutrient requirement of the soil in the area since agriculture is the main occupation of these rural dwellers. According to Agbenin (1998) most of the fertilizers applied in Nigerian soils can contain some metals such as Cu, Fe, and Pb. The fifth component in the shaly soils relates to Pb-Zn mineralization weathering associated with the area.

TABLE 13: Principal component analysis for calcareous soils at (0-30 cm) depths

Parameter	Components		
	PC 1	PC 2	PC 3
pH	-0.460	0.854	-0.071
OM	-0.963	0.055	0.256
Ca	0.334	-0.290	-0.022
K	0.064	0.334	0.939
Al	0.983	-0.011	0.134
Na	-0.020	-0.937	-0.193
Fe	0.082	0.937	-0.63
Cu	-0.780	0.316	-0.529
Zn	0.222	-0.348	0.842
Pb	0.089	-0.035	-0.965
Co	0.712	0.688	-0.017
Mo	0.915	0.046	0.154
% Variance	35.324	28.755	24.615
Cumulative %	35.324	64.079	88.694

Extraction method: Principal component analysis A 3 components extracted

TABLE 14: Component analysis for shaly soils at (0-30 cm) depth.

Parameters	Components				
	PC 1	PC 2	PC 3	PC 4	PC 5
pH	-0.220	0.238	0.119	0.841	0.008
OM	0.104	-0.066	0.861	0.239	0.312
Ca	0.033	-0.008	-0.826	0.58	0.201
K	-0.259	-0.704	0.67	0.055	-0.269
Al	-0.345	0.855	-0.014	-0.103	0.036
Na	-0.024	0.824	0.145	0.458	-0.003
Fe	0.882	-0.221	0.054	-0.251	-0.287
Cu	0.752	0.099	0.074	-0.566	-0.070
Zn	-0.061	0.235	-0.009	-0.122	0.965
Pb	-0.099	-0.243	-0.063	0.564	0.748
Co	0.608	-0.583	0.401	-0.316	0.029
Mo	-0.742	0.135	0.473	-0.238	-0.293
% Variance	21.035	20.814	18.139	15.537	15.501
Cumulative %	21.035	41.489	59.988	75.525	91.026

Extraction method: Principal Component Analysis. A five component extracted.

Enrichment factor (Ef): This was used to quantify the proportion of heavy metal enrichment by comparing the concentration of specific element in the crust or background value (Adamu et al., 2003) Kabata-Pendias (1993), agrees that enrichment is a better assessment of on site contamination than maximum allowable concentration because enrichment factors takes into account the geologic variation of elemental abundance of rock types and mineralization, cultural practices and probably human induced changes. Ef is usually calculated with respect to Al, Fe, Ti or Zn because these elements are relative immobile. Fe was selected as reference element in this study and background values according to Wedepohl, (1971) were used to compute for the various metals. The mean values of the metals were used in the computation using the formula;

$$Ef == \frac{Cx/Fe\ Sample}{Cx/Fe\ background}$$

Where Ef = enrichment factor
Cx = Concentration of metals for which enrichment factor is calculated.

Table 15: Enrichment factor and Normal range of metals in soils of the study area.

parameter	Mean in value in shaly soils	Mean value calcareous soils	Normal range	Ef for shaly soils	Ef for calcareous soils	Background value (ppm)
Ca%	1.56	2.76	NA	0.98	1.73	1.60
K%	2.58	1.38	NA	0.97	0.52	2.66
Al%	6.61	3.22	NA	0.75	0.37	8.80
Na%	0.90	1.71	NA	1.52	2.90	0.59
Fe%	5.25	2.35	0.5-4.3	1.11	0.50	4.72
Cu mg/kg	117.95	59.90	2-100	2.62	1.33	45.00
Zn mg/kg	357.00	205.50	10-300	3.76	2.16	95.00
Pb mg/kg	176.15	46.10	10-100	8.81	2.31	20.00
Co mg/kg	90.10	70.00	0-8	4.74	3.68	19.00
Mo mg/kg	23.85	67.60	0-5	7.95	22.38	3.00

NA –Not available
Background values of metals after Wedepohl, (1971).
Normal range in soil after Brady and Weil, (1996).
Sutherland (2000), categorized contamination based on enrichment factor (EF) into five categories.
Ef < 2 = deficiency to minimal enrichment
Ef 2 – 5 = Moderate enrichment
Ef 5-20 = Significant enrichment
Ef 20 – 40 = Very high enrichment
Ef >40 = Extremely high enrichment

According to the author, increase in enrichment factor values suggest contribution from anthropogenic activities. Where enrichment factor is less than 1.5, it suggests the metal concentration may be due to natural processes such as weathering and influence of organic matter. Enrichment factor greater than 5, suggest contamination by a particular heavy metal (Harikumer and Jisha 2010). A close look at table 15, reveals deficiency to minimal enrichment for Al, Ka, Ca, Fe and Na. Cu, Zn and Co show moderate enrichment while Mo and Pb indicate significant enrichment for soils in the shaly area. Calcareous soils reveal deficiency to minimal enrichment for Al, Fe, Cu, and Ca, Na, Zn, Pb and Co show moderate enrichment and only Mo indicated very high enrichment. The minimal enrichment of calcium in the calcareous soils is due to the acidity of the soils.

CONCLUSION

In conclusion, indication from the enrichment factor (Ef) values shows that soils of the area have been minimally, moderately, significantly and highly contaminated with metals studied. The study relates with the fact that uptake and phyto accumulation of major and trace metals depends on plant parts. These assessment also confirms that where negligible concentration of major and trace metals occur in soil or agricultural materials, plants will take up such metals when ever present hence there is positives role of soil column and vegetation in the removal and accumulation of these metals in different parts of cassava plants from the different parts and the different ratios computed.

The area is rural and a greater percentage of the inhabitants are farmers. Here land is seriously cultivated and animals are reared for food production. These animals feed directly from the local grown crops and these metals are ingested into their system from these unwashed crops.

The inhabitant of the area feed from the crops grown in the area, example cassava tubers for processing garri and cassava leaves fried and used for eating yam.

Although, no adverse health effect have yet been observed, long term metals exposure by regular consumption of locally grown vegetable may posses potential health problems to animals and human living in the area where enrichment and contamination factor indicates significant enrichment for shaly soils (Pb and Mo) and very high enrichment for calcareous soils (Mo). Constant monitoring of the concentrations of Pb, Mo, Cu, Zn and Co is recommended to prevent potential pollution risk in the future.

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