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INORGANIC POLLUTANTS IN VEGETABLES OBTAINED FROM SELECTED FARMLANDS IN MILLENNIUM CITY AND UNGUWAN KUDU OF KADUNA STATE

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Abstract
Inorganic pollutants are substances that are mostly of mineral origin, with metals and salts that exist naturally in the environment but have been altered by human anthropogenic activities thereby increasing their numbers, pervading the environment and becoming toxic due to accumulation in food chain. This research studied the determination and comparison of the levels of inorganic pollutants in vegetables obtained from selected farmlands in Millennium City and Unguwan Kudu, Kaduna State. 16 composite vegetable samples (lettuce and spinach) were collected twice between August and December, transported to the laboratory and prepared for determination of inorganic pollutants. The levels of inorganic pollutants were determined and compared with acceptable international standards (NSDWQ and WHO). The inorganic pollutants in vegetables (Spinach and Lettuce) were found to be higher in NO_3 (23.15±0.05) mg /kg and the least was observed in Hg (0.003±0.00) in spinach of U/Kudu and MC respectively also negative value was obtained in Pb. Each inorganic pollutants were observed to be significantly different across the sampling sites except in some cases. Heavy metals such as Cu in study sites could be due to electric wiring, plumbing materials, adornments, coins and composites that are present in the environment. When compared with the permissible limit of NSDWQ and WHO, some of the inorganic pollutants in vegetables were above the permissible limit, while others were observed to be within the permissible limit and the inorganic elements in lettuce were generally found to be more than that in spinach for the months of August and December from U/Kudu and MC respectively.

Keywords: Inorganic pollutants, Vegetables, Millennium City, Unguwan Kudu, NSDWQ, WHO, Heavy metals.

Introduction

Minerals, organic and inorganic are essential for human growth and development, although minerals of inorganic origin have been identified to be a source of inorganic pollutants. These include metals and salts existing naturally in our immediate environment altered by anthropogenic activities like mining, drainage construction, metallurgical and chemical processes thereby increasing their numbers, pervading the environment and becoming toxic due to accumulation in food chain (Sharma and Walia, 2016). The existence of inorganic pollutants litters the environment in all its compartments and comprise much of the contamination at sites worldwide. Some factors responsible for the introduction of these pollutants are industrial, agricultural and domestic wastes that further cause adverse harm to humans and the health of living things (Singh *et al.*, 2010). Minerals have been identified to be present in both body tissues and fluids. Their presence aids maintenance of certain essential life processes, these minerals which are chemical constituents are used by the body in several ways. (Eruvbetine 2003; Soetan *et al.*, 2010). Every form of living matter requires these inorganic elements for their normal life processes (Ozcan, 2003). There are three classifications of minerals, these are macro (major) (eg. phosphorus, calcium, chloride and sodium), micro (trace) (eg. copper, iron, cobalt, magnesium, potassium, iodine, manganese, zinc, molybdenum, chromium, fluoride, selenium and sulfur) and ultra-trace elements. (Eruvbetine, 2003). Also, some heavy metals have been identified to be essential for plant growth in traces or relatively lower quantities. Rock weathering and anthropogenic activities are implicated to be responsible for the presence of heavy metals in surface water (Okweye, 2013). Using sewage water for irrigation over a long period of time contaminates both soil and vegetables, causing toxicity and deterioration respectively with considerable amount such heavy metals like Cu, Cr, Fe, Pb, Cd and Zn (Wuana and Okieimen, 2011).

It has been identified that different weathering processes such as biochemical, mechanical and biological processes aid the release of heavy metal into the environment accompanied by human activities. These factors are implicated to cause heavy metal contamination which accumulates within living organisms in food chain (Koivula *et al.,* 2011; Gupta *et al.,* 2021). These heavy metals by some means diffuse into the different parts of the earth such as soil, air and water bodies from where plants take them up (Proshad *et al.,* 2019; Kharazi *et al.,* 2021). It is very difficult to remove heavy metals from living organism once they have entered it, they are rather cycled within the food web and sometimes can become hyper accumulated (Seema *et al.,* 2022). Hyper-accumulated plants provide nourishment for both humans as well as animals based on the amount of these heavy metals in them and the type. Excess intake of heavy metals has been identified to cause several negative impacts for both animals and humans alike. Ingesting heavy metals that are accumulated in vegetables pose potentially harmful health risks such as cancer and kidney impairment to life forms (Chen *et al.,* 2021; Seema *et al.,* 2022)

This study aimed to determine the presence and concentration of inorganic pollutants in vegetables obtained from farmlands in the study area.

Materials and method

Study area

The research was conducted in Millennium city and Unguwan Kudu of Kaduna State, North-West, Nigeria, with the following co-ordinates (10° 32′41.4"N, 7° 29′05.6"E) and (10°31′20.6"N, 7°27′59.2"E) respectively. Millennium city is located at Chikun Local Government Area, has an area of 4,645 km^2 and a population of 368,250, while Unguwan Kudu is located at Kaduna North Local Government Area, and has an area of 72km^2 and a population of 357,694 as at the 2006 census. These two locations are predominant for irrigation farming which are crops, vegetable farming and cassava cultivation etc. supplying vegetable products to the inhabitants and its environs. The sources of irrigation water on the site include potable (pipe-borne) water and wastewater from shallow (approximately 1meter deep) hand dug wells and stream which serves as a source of irrigation water for the farmers, as well as water for domestic purposes for nearby populations. The types of crops grown on the site include; lettuce, spring onions, spinach, carrots and cabbage etc (Idoko *et al.*, 2016).

Vegetable sample collection

16 composite vegetable samples (lettuce and spinach) were collected twice between August and December labelled as MC for Millennium City and U/Kudu for Unguwan Kudu. (Malan *et al.*, 2015; Idoko *et al.*, 2016) then labelled and were stored in plastic bags. All the samples were taken to laboratory for processing and analysis.

Determination of Inorganic Pollutants

Determination of Magnesium in vegetables.

0.5 g of vegetable samples were put in a beaker, diluted to 50mL. 10mL of Na2O4 solution and 15mL of buffer solution was added, and the solution was heated slowly on hot plate and filtered, the precipitate was wash with 40 mL of water containing 2 mL buffer solution and put into titration flask. Ten drops of eritrochrome black T indicator and 2 mL triethanolmine and was titrated with EDTA to a clear blue with no trace of red in solution. Finally, a blank titration was carried out in the same manner and subtracted from the sample reading to determine concentration (Ademoroti, 1996; Singh, 2001)

Calculation:

50 mL of EDTA solution were required for titration

$$\frac{\text{Mg } (50\ \text{mgkg}^{-1}) - 10(\text{mL}) \times \text{volume of solution}}{10 \times \text{aliquot} \times \text{sample wt (g)}}$$

Determination of Calcium Vegetables.

0.5 g vegetables sample were put in a beaker, diluted to 50mL of Na2O4 solution and 15mL of buffer solution was added, and the solution was heated slowly on hot plate and filtered, the precipitate was wash with 40 mL of water containing 2mL buffer solution and put into titration flask. 10 drops of Eretrochrome black T indicator and 2mL trithanolmine and was titrated with EDTA to a clear blue with no trace of red in solution. Finally, a blank titration was carried out in the same manner and subtract from the sample reading to determine concentration (Ademoroti, 1996; Singh, 2001)

Calculation:

50 mL of EDTA solution were required for titration

$$\frac{\text{Ca } (50\ \text{mgkg}^{-1}) - 10(\text{mL}) \times \text{volume of solution}}{10 \times \text{aliquot} \times \text{sample wt (g)}}$$

Determination of nitrate in Vegetables

Nitrate analyzed in vegetable samples were carried out using smart Spectrophotometer (LaMotte, 2000). Vegetable samples solutions chopped into smaller sizes. A measured amount, 1 g was transferred into 100 ml flask containing 50 ml of distilled water, covered with a lid and allowed to shake for 30 minutes, then filtered into another 100 ml volumetric flask and the volume made to the mark with distilled water following the procedure of Radojevic and Bashkin (1999). Nitrate was determined using standard cadmium reduction method 3649 – SC (Rupa et al., 2003).

Determination of Phosphate in Vegetables

Each vegetable sample was chopped into small pieces and air dried. Dried samples were grounded and sieved with mesh size 1 mm. a weighing balance was used to weigh 1 g of each sample into acid-washed porcelain crucibles. Magnesium acetate, 5 ml of 20% (w/v) was added and evaporated to dryness. Other processes followed the method presented by Radojevic and Bashkin (1999) without modification.

Determination of Potassium in Vegetable

0.5g vegetable sample were put in a beaker, diluted to 50mL of Na2o4 solution and 15mL of buffer solution was added, and the solution was heated slowly on hot plate and filtered, the precipitate was wash with 40 mL of water containing 2 mL buffer solution and put into titration flask. 10 drops of Eretrochrome black T indicator and 2 mL trithanolmine and was titrated with EDTA to a clear blue with no trace of red in solution. Finally, a blank was preparing, then concentration of potassium was determine by Uv spectrophotometer (Singh, 2001; Wuana *et al.*, 2015).

Vegetable samples preparation for heavy metal determination

The vegetable samples collected from the experimental sites were taken to the laboratory where they were washed and rinsed with deionized water. They were carefully chopped into smaller portions (root, stem and leave) with a clean stainless steel knife. The chopped vegetable samples were air dried and reduced in size by pounding to a fine powder using cleaned mortar and pestle. The samples were sieved using 2mm plastic sieve and stored in a labelled container prior to analysis at the Kaduna Environmental Protection Authority (KEPA) Laboratory as previously (Idoko, *et al.*, 2016; Idoko, *et al.*, 2018).

Digestion of plant samples for heavy metals analysis

Vegetable samples were weighed to obtain 1 g and placed in 50 cm^3 beakers separately, 10 cm^3 concentrated HNO_3 was added to each beaker. Samples were heated on hot plate until the solution becomes partly dried, 10 cm^3 of concentrated HNO_3 was added. The solution was kept on a hot plate for 1 hour to allow for the formation of a clear suspension. The mixture was allowed to cool and filtered through filter paper. The solution was then transferred to a 50 cm^3 volumetric flask and de- ionized distilled water added to its mark (Huang *et al.*, 2004; Hseu, 2004; Narin *et al.*, 2004).

Data analysis

Data analysis was carried out with statistical package for social sciences (SPSS) version 23. Mean and analysis of variance (ANOVA) were employed to assess significant differences ($P \leq 0.05$) in the different data collected across different sites. Duncan's multiple range test (DMRT) was utilized to distinguish varying means.

Results and discussion

The result shows a clear-cut difference of inorganic pollutants in vegetables between spinach and lettuce for the months of August and December at MC (Table 1). Across the two months therefore, lettuce had 8.27±0.01, 10.35±0.05 and 23.15±0.10 significant amount of K, $^{PO}{}_4$ and $^{NO}{}_3$ which are the highest recorded while the lowest 2.23±0.00, 1.46±0.01 and 7.25±0.05 were observed in lettuce and spinach within the months of August and December, although the amount of K was low in the month of December yet there was a significant difference ($p \geq 0.05$) between spinach and lettuce. Unlike the result of K, spinach had the highest record of 10.12±0.00 for Ca in the month of December and the lowest in August. It is important to note that Ca was generally higher in spinach and lettuce in the month of December. Spinach had the highest amount of Mg (1.94±0.00) and Cu (1.58±0.00) at MC while lettuce had 0.63±0.00 and spinach had 0.15±0.00 at U/Kudu which are the lowest (Table 4), but when compared between the two months December recorded the highest and August the lowest. The amount of Pb (0.21±0.00) and Cd (0.46±0.00) were higher in lettuce in the month of December than in August and lower in spinach in the same month. Spinach had more amount (0.98±0.00) of Zn in December while lettuce had the least (0.27±0.00) in August which is the lowest for the two months. Finally, lettuce (0.02±0.00) had more Hg in both months than spinach (0.003±0.00) (Table 1 and 2).

The number of pollutants on vegetables in MC indicates more K, and NO_3 in lettuce in the month of December than in spinach in the same months (Table 2). The quantity of K was significantly higher (8.27±0.00) in lettuce and lower (2.32±0.00) in same month (Table 4) also when compared with the concentration in August (Table 1). PO4, in Lettuce had 6.27±0.01 which was significantly higher in August and 1.46±0.01 was observed in spinach in the same month. The amounts of Ca were higher (i.e. 10.12±0.00 and 9.06±0.00) in December in both spinach and lettuce of U/Kudu than in the month of August. The result of Mg indicates 0.92±0.00 in spinach in the month of August and 0.48±0.00 in lettuce of MC in the same month as the highest and lowest amounts for the months of August. (Table 1).

There was no Pb obtained in spinach and lettuce in August while small amount were found in the same vegetables in December. Finally, the amount of Cd, Cu and Hg indicated that lettuce had 0.38±0.00, 0.16±0.00 and 0.004±0.00 respectively which are higher in August at U/Kudu and NMC and comparable or equal values in December and low amount in spinach in both months (Table 2).

Table 1: Mean concentration (mg/kg) of Inorganic Pollutants in Spinach and Lettuce of MC and U/Kudu in August

	Millennium city		Unguwan kudu		F-value	P-value
	Spinach	Lettuce	Spinach	Lettuce		
K	6.44±0.00 b	3.81±0.00 c	6.78±0.00 a	3.76±0.00 d	568.67	0.000
PO4	1.46±0.01 d	6.27±0.01 a	1.92±0.01 c	4.27±0.01 b	8412.74	0.000
NO3	23.15±0.05 a	16.00±0.00 d	21.16±0.01 b	17.15±0.05 c	8967.34	0.000
Ca	1.09±0.00 d	2.05±0.00 c	8.31±0.01 b	9.02±0.00 a	7391.92	0.000
Mg	0.92±0.00 a	0.48±0.00 d	0.53±0.00 c	0.82±0.00 b	738.91	0.000
Pb	0.00±0.00 e	0.00±0.00 e	0.05±0.00 a	0.03±0.00 b	834.73	0.000
Zn	1.33±0.00 c	1.05±0.00 d	2.35±0.09 a	2.13±0.00 b	155.92	0.000
Cd	0.36±0.00 b	0.38±0.00 a	0.36±0.00 b	0.38±0.00 a	2475.43	0.000
Cu	0.15±0.00 b	0.16±0.00 a	0.14±0.00 c	0.16±0.00 a	1234.29	0.000
Hg	0.003±0.00 b	0.004±0.00 a	0.003±0.00 b	0.004±0.00 a	121.00	0.000

Superscripts with different letters are significantly different at p≤0.05

Key: SE = Standard Error, Mg/L = milligrams per litre, Mg/kg = milligrams per kilogram, PO4= phosphates, NO3 = nitrates, Ca = calcium, Hg = mercury, Pb = lead, Zn = zinc, Cd = cadmium, Cu = copper, Hg = mercury

Table 2: Mean concentration (mg/kg) of Inorganic Pollutants in Spinach and Lettuce of MC and U/Kudu in December

	Millennium city		Unguwan kudu		F-value	P-value
	Spinach	Lettuce	Spinach	Lettuce		
K	2.82 ± 0.01^{c}	8.27 ± 0.01^{a}	2.98 ± 0.00^{b}	2.32 ± 0.00^{d}	4375.23	0.000
PO4	2.67 ± 0.01^{d}	10.35 ± 0.05^{a}	3.28 ± 0.01^{b}	3.02 ± 0.01^{c}	2115.34	0.000
NO3	8.15 ± 0.05^{c}	14.60 ± 0.10^{a}	7.25 ± 0.05^{d}	9.65 ± 0.05^{b}	2456.14	0.000
Ca	2.00 ± 0.00^{d}	3.35 ± 0.00^{c}	10.12 ± 0.00^{a}	9.06 ± 0.00^{b}	4532.38	0.000
Mg	1.94 ± 0.00^{a}	1.67 ± 0.00^{b}	0.89 ± 0.00^{c}	0.63 ± 0.00^{d}	5289.37	0.000
Pb	0.00 ± 0.00^{e}	0.00 ± 0.00^{e}	0.03 ± 0.00^{c}	0.12 ± 0.00^{b}	7834.67	0.000
Zn	0.71 ± 0.00^{b}	0.27 ± 0.00^{d}	0.98 ± 0.00^{a}	0.69 ± 0.00^{c}	7623.83	0.000
Cd	0.35 ± 0.01^{d}	0.46 ± 0.00^{a}	0.36 ± 0.00^{c}	0.39 ± 0.00^{b}	394.88	0.000
Cu	1.58 ± 0.00^{a}	0.17 ± 0.00^{b}	0.15 ± 0.00^{c}	0.17 ± 0.00^{b}	5623.57	0.000
Hg	0.01 ± 0.00^{b}	0.02 ± 0.00^{a}	0.01 ± 0.00^{b}	0.02 ± 0.00^{a}	1299.00	0.000

Superscripts with different letters are significantly different at $p \leq 0.05$
Key: SE = Standard Error, Mg/L = milligrams per litre, Mg/kg = milligrams per kilogram, PO4= phosphates, NO3 = nitrates, Ca = calcium, Hg = mercury, Pb = lead, Zn = zinc, Cd = cadmium, Cu = copper, Hg = mercury

Each inorganic pollutants and pH were observed to be significantly different across depth and month except in some cases where there were no significant differences. When compared with the permissible limit by NSDWQ and WHO, these pollutants were within acceptable limit, making it not poisonous or having the tendency to impact negative effect during consumption. The concentrations of cadmium in both U/Kudu and MC were observed to be above the permissible limits of the WHO and NSDWQ. The increased cadmium concentrations may be due to battery waste water deposited directly or indirectly into the water, mining and smelting operations, electroplating, plastic stabilizers, and fertilizers (Rahmanian *et al.*, 2015). Due to their persistence and cumulative tendency in the environment as well as their associated toxicity, it is considered to be a serious threat to the environment and human health (Banwo, 2006). At- risk population due to cadmium toxicity includes the elderly, infants and women in their reproductive age. These set of individuals have very low body iron stores, and cadmium absorption and retention have been reported to be inversely related to body iron status (WHO, 2008). The principal sources of nitrates include the use of nitrogen-based fertilizers, domestic sewage, animal dung, ammonia, and urban wastes (Tedesse *et al.*, 2018). The present study reported higher amount of nitrates in vegetables which is indicative of certain agricultural activities and other anthropogenic factors. Although nitrate is an important source of nutrient for humans and livestock, a higher dosage as reported in the study can cause methamoglobinemia in infants which can result in coma and death probably while in adults, it can lead to diuresis and haemorrhage of the spleen (Ekhator *et al.*, 2015). The findings are not consistent with those reported by Kazaure *et al.*, (2019) because the water they observed was treated. This is indicative that treated water reduces the amount of nitrate present.

Phosphate in water and plants alike are influenced by certain factor like location, degree of agricultural and industrial activities within the vicinity, rock type of the area, topography of the rainfall pattern, climate nature and frequency of sampling, biological activities in soil, atmospheric deposition and chemical weathering of bedrock, flow rate and proximity to ground water (for surface water) and top soil type and depth (for groundwater bodies (Letif *et al.*, 2018). These factors may have been responsible for the discrepancies of phosphates level in water as presented in the results. Although there is no nutritional basis for the regulation of phosphates level, it is important to control eutrophication in the ecosystem though (Nolan, 2008). The observation that all the analysed samples have PO_4 is indicative of significant anthropogenic impute from domestic sewage, agricultural and industrial practices in addition to natural sources of rock weathering and phosphate cycles in water. All vegetable samples had PO_4 levels exceeding the maximum acceptable level PO_4 for prevention of eutrophication, it is obvious that the water in U/Kudu and MC are already under hypereutrophic state. This report is similar to that of Fadiran et al. (2007) who reported more phosphates in surface water during their research. Magnesium is important because it enhances proper functioning of living organisms, although high concentration of magnesium gives laxative effect (Airaodion *et al.*, 2019). It is easily found in minerals like dolomite and magnetite and it contributes to the hardness of water used for both agricultural and domestic purposes (Shawai *et al.*, 2018). The report in this study is in sync with the report of Ekhator et al. (2015) in a survey in Edo state, Nigeria. The permissible limit for magnesium was not exceeded making vegetables in U/Kudu and MC harmless during and after consumption. Zinc plays important role in the metabolism and gene expression of living organisms (Nyamukamba *et al.*, 2019). High amounts of zinc in the body may induce vomiting, dehydration, abdominal pain, lethargy and dizziness. Other physiological dysfunctions associated with zinc intoxication are impaired copper utilization, sense of smell and taste, brain function and growth (Olayinka *et al.*, 2107; Tedesse *et al.*, 2018; Chika and Prince, 2020). The present study reveals the mean concentration of Zn in water at MC and U/Kudu to be within the permissible limits. The result agrees with that of Aloke *et al.*, (2019) and Jagaba *et al.*, (2020) who reported similar concentrations of Zn tested samples. Zinc exist in very low concentrations in nature due to its restricted mobility from site of weathering, however, zinc may accumulate in the environment due to human and industrial activities such as engine wear, exhaust fumes, waste incineration and use of sewage sludge as fertilizers (Nyamukamba *et al.*, 2019). Copper (Cu) is a fundamental supplement for humans and other living organisms although it is needed in a little amount for enzymes functioning and sugars breakdown. In vertebrates, its capacities are to move hemoglobin and haemocyanin oxygen molecules in the blood (WHO, 2011). The amount of Cu present in water of U/Kudu and MC were found to be within the permissible limit making it not poisonous. The source of Cu in U/Kudu and MC may be due to electric wiring, plumbing materials, adornments, coins and composites (Solomon, 2009). This result therefore is similar to the report of Tom-Petersen *et al.*, (2011) who observed that smaller concentration of Cu can inhibit bacterial growth and development.

Conclusions

The inorganic pollutants in vegetables some were observed to be within the permissible limit and others were above the limit, the inorganic elements in lettuce were generally found to be more than that in spinach for the August and December from U/Kudu and MC.

Recommendations

This research suggests the regular scrutiny of inorganic pollutants in vegetables; to avoid heavy metals accumulation and further transfer in food chain. Efforts should be made at increasing public awareness on the level of inorganic pollutants in U/Kudu and MC area of Kaduna State. Efforts to mitigate the concentration of Pb, Hg and Cd should be carried out due to the organ related toxicity associated with ingestion of trace elements in food chain.

Conflict of interest. Authors declare that there is no conflict of interest

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