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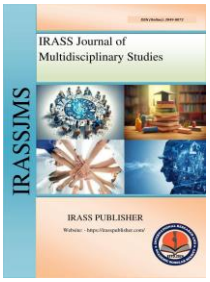

Comparative Study of Inorganic Pollutants in Soils Obtained From Selected Farmlands in Millennium City and Unguwan Kudu, Kaduna State, Nigeria

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Abstract: Inorganic pollutants are usually substances of mineral origin, with metals and salts that are found 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 soils obtained from selected farmlands in Millennium City and Unguwan Kudu, Kaduna State. Soils were collected at depths (0-15cm and 15-30cm) for the months of August and December, transported to the laboratory and prepared for determination of inorganic pollutants and pH as well. The levels of inorganic pollutants were determined and compared with acceptable international standards (NSDWQ and WHO). pH concentrations of soils in the month of August were at the alkaline range while neutral range was observed in December except at 15- 30cm depth at U/Kudu that was at alkaline range. The number of inorganic pollutants in soil of MC and U/Kudu for the month of August and December had higher concentrations in NO_3 (16.60±0.10 and 14.60±0.10) mg/kg and (15.01±0.00 and 12.29±0.22) mg/kg respectively at the same depth of 15-30cm and lowest concentrations was observed in Hg. Each inorganic pollutant was observed to be significantly different across the two sampling sites except in some cases where there were no significant differences. When compared with the permissible limits of NSDWQ and WHO, some of the inorganic pollutants in the soils were above the permissible limit while pH was within the limits. The farmlands therefore might not be good for agricultural purposes, as they contain higher concentrations of some inorganic pollutants such as (Pb, Cd and Hg).

Keywords: Inorganic pollutants, soil pollution, heavy metals, farmland fertility, NSDWQ, WHO

1.0 Introduction

Inorganic pollutants are usually substances of mineral origin, with metals and salts that are found naturally in the environment but have been altered by human anthropogenic activities such as mining, drainage, smelting, metallurgical and chemical processes thereby increasing their numbers, pervading the environment and becoming toxic due to accumulation in food chain (Sharma and Walia, 2016). Inorganic pollutants have pervaded the environment in all its compartments and comprise much of the contamination at sites throughout the world. Industrial, agricultural and domestic wastes contribute to environmental pollution, which causes adverse harm to human and animal health (Singh *et al*., 2010). Minerals are inorganic substances, present in all body tissues and fluids and their presence is necessary for the maintenance of certain physicochemical processes which are essential to life, minerals are chemical constituents used by the body in many ways. Although

they yield no energy, they have important roles to play in many activities in the body (Eruvbetine 2003; Soetan *et al*., 2010). Every form of living matter requires these inorganic elements or minerals for their normal life processes (Ozcan, 2003). Minerals may be broadly classified as macro (major) or micro (trace) elements and third category is the ultra-trace elements. The macro-minerals include calcium, phosphorus, sodium and chloride, while the micro-elements include iron, copper, cobalt, potassium, magnesium, iodine, zinc, manganese, molybdenum, fluoride, chromium, selenium and sulfur (Eruvbetine, 2003). Also, heavy metals are inorganic elements essential for plant growth in traces or very small quantities. The presence of heavy metals in surface water is caused by weathering of soils, rocks and by anthropogenic activities that disturb the natural distribution of heavy metals in surface water (Okweye, 2013). Long term use of sewage water for irrigation contaminates the soil and vegetables to such extent that it becomes toxic to plants and causes the deterioration of the soil that contains considerable amount of potentially harmful substances of heavy metals like Cr, Fe, Cu, Pb, Zn and Cd (Wuana and Okieimen, 2011).

Therefore, this study was done to determine the concentration and compare the level of inorganic pollutants in soils obtained from farmlands in the study area.

2.0 Materials and Methods

2.1 Study area

The research was conducted in Millennium city and Unguwan Kudu of Kaduna State, North-West, Nigeria, with the following co-ordinates (10^o 32´41.4"N, 7^o 29´05.6"E) and (10^o31´20.6"N, 7^o27´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, 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.

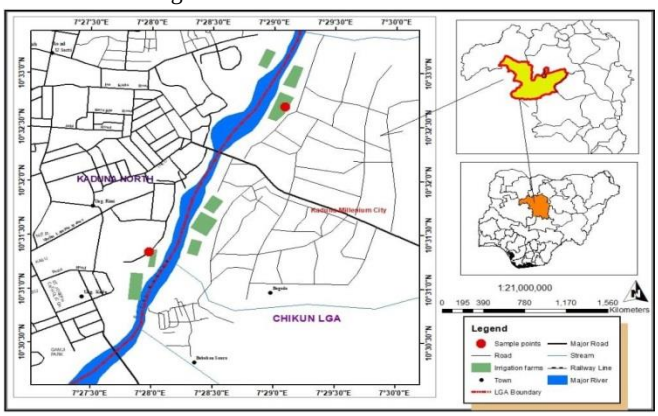

Figure 1.0: GPS Map of Millennium City (Chikun LGA) and Ungwan Kudu (Kaduna North LGA)

2.2 Sample Collection

About 1 kg of composite soil samples were collected from the two sampling sites with the aid of a soil Augar at surface 0- 15 cm and sub-surface 15-30 cm for the months of August and December, labelled as MC for Millennium City and U/Kudu for Unguwan Kudu. These soil samples of 0 – 15 cm were composed together to produce a single composite sample and soil samples of 15-30 cm were also composed together to produce a single composite sample. The sampling depth of 0–15 cm was chosen based on the most active zone of maximum root concentration and the most sensitive zone of erosion and atmospheric (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.

2.3 Determination of Inorganic Pollutants and pH

2.3.1 Determination of pH

Standard buffer solution (pH 4 and 7) was used and 20g of 2mm sieved soil samples was weighed into 200mL beaker; distilled water was added gradually down the side of the beaker to enable it passes through the microspores, the mixtures were mixed thoroughly to ensure homogeneity and allowed to stand for 15 min, the electrode was placed in the liquid and pH of solution was taken at the stability of the meter Ademoroti (1999), Rupa *et al*., (2003). Wuana *et al*., (2015)

2.3.2 Determination of Magnesium in Soil.

1g of soil sample was put in a beaker, diluted to 50mL. 10mL of Na_2O_4 solution and 15mL of buffer solution was added, and the solution was heated slowly on hot plate and filtered, the precipitate was washed 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 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

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

2.3.3 Determination of Calcium in Soil

1g of soil sample was put in a beaker, diluted to 50mL. 10mL of Na_2O_4 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 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

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

2.3.4 Determination of nitrate in Soil

The concentration of nitrate analysed in each of the soil samples were carried out using smart Spectrophotometer (LaMotte, 2000). 1g of soil sample and 50mL water sample were transferred into 100ml flask and soaked with 50ml of distilled water. The flask was capped and shaken for 30 minutes, then filtered into another 100ml volumetric flask and the volume made to the mark with distilled water (Radojevic and Bashkin, 1999). Nitrate was determined spectrophotometrically using standard cadmium reduction method 3649 – SC (Rupa *et al*., 2003), while Nitrite was determined using standard diazotization method 3650 – SC (Ademoroti, 1996; Rupa *et al*., 2003).

2.3.5 Determination of Phosphate in Soil

Each of the soil samples were air-dried, grounded and sieved with a sieve of mesh 1mm. A known amount (1g) of each of the ground and sieved samples were weighed into acid-washed porcelain crucibles. Five (5) ml of 20% (w/v) magnesium acetate were added and evaporated to dryness. The crucibles were then transferred into the furnace at 5000^{o}C for four (4) hours, removed and cooled in desiccators. Ten (10) ml of 6M HCl were then added to each of the crucible and covered, then heated on a steam bath for fifteen minutes. The contents of each crucible underwent acid digestion on a hot plate. After digestion, 1ml of concentrated HNO_3 was added to soil digest. The heating was made to continue for 1 hour to dehydrate silica. 1ml of 6M HCl was then added, swirled and then followed by the addition of 10ml distilled water and again heated on the steam bath to complete dissolution. The contents of the evaporating basins were cooled and then filtered through a Whatman no.1 filter paper into 50ml volumetric flasks and the volumes made up to the marks with distilled water. Phosphate was determined using Hach Direct Reading 2000 Spectrophotometer. (Radojevic and Bashkin, 1999).

2.3.6 Determination of Potassium in Soil

1g of soil sample was put in a beaker, diluted to 50mL. 10mL of Na_2O_4 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 prepared, the concentration of potassium was determined by Uv spectrophotometer (Singh, 2001; Wuana *et al*., 2015).

2.4 Soil sample preparation for heavy metals determination

The soil samples were oven dried at 105°C for 24 hours, followed by grinding and sieving using 0.18 mm sieve. A 0.5 g each of dry soil was poured into a graduated test tube and mixed with 2 mL of aqua regia 1:3 (1 conc. HCl: 3 conc. HNO_3). The mixture was digested on a hot plate at 95°C for 1 hour and allowed to cool to room temperature. The sample was diluted to 10 ml using distilled water and left to settle overnight. The supernatant was filtered prior to heavy metal analysis using AAS as adopted by Idoko *et al*., (2016) and Idoko *et al*., (2018).

2.5 Digestion of soil samples for heavy metal analysis

The air-dried samples (2.5 g) were transferred into a pyrex beaker and mixed with 10 cm^3 of aqua regia, which consisted of HCl: HNO_3 (3:1). The mixture was digested on a hot plate at 95 °C for 1 h and allowed to cool to room temperature. The resultant mixture was diluted to 50 cm using deionized distilled water and left to settle (Mwegoha and Kihampa, 2010). The supernatant was filtered through filter paper prior to analysis by Atomic Absorption Spectrometry

3.0 Results and discussion

The results show the comparative determination of inorganic pollutants in soils obtained from selected farmlands in millennium city and Unguwan Kudu, Kaduna.

All elements were compared with the permissible limit provided by WHO and NSDWQ. The permissible limits for pH and each inorganic pollutants include; pH (6.5-8.5), K (20 mg/L), PO4 (0.10 mg/L), NO3 (50 mg/L), Ca (7.5 mg/L), Mg (20 mg/l), Pb (0.01 mg/L), Zn (3 mg/L), Cd (0.003 mg/L), Cu (1mg/L), and Hg (0.001 mg/L).

The result obtained for the month of August showed a comparable pattern of increased pollutants from 0 cm – 15 cm to 15 cm – 30 cm except in the case of Pb, Cd, Cu and Hg (Table 1). The result reveals that U/Kudu at a depth of 15 cm – 30 cm had pH and PO4 of 8.27±0.01 and 10.35±0.05 which are highest while 7.74±0.01 and 3.04±0.01 were observed in MC at 0 cm – 15 cm depth respectively. Observed results shows that NO3, Cd and Hg (i.e. 16.60±0.10, 0.52±0.00 and 0.02±0.00 respectively) were higher on MC soil between 0 cm – 15 cm and 15 cm – 30 cm but lower on the soil of U/Kudu (Table 1).

Generally, the data observed in the result indicates clear cut differences between depths of 0 cm – 15 cm and 15 cm – 30 cm (Table 2). The result obtained for the samples exhibited similar pattern and compares very closely to both figures obtained on 0 cm – 15 cm depth for MC and U/Kudu. Similar pattern was observed but with slight difference at 15 cm – 30 cm (Table 1). Soil in NMC had the same pH of 7.02±0.01 at December while soil in U/Kudu had slightly higher pH in the same month with 8.07±0.00 at 15 cm – 30 cm depth (Table 2). Unlike the result for pH, the results for PO4 was higher and compares closely at the depth of 15 cm - 30 cm, although the soil in U/Kudu recorded more phosphates (i.e 8.80±0.10) while the soil in MC recorded 2.03±0.01 which is the lowest in the two sites. The amount of NO3 in the soil was higher in depths of 15-30cm in the month of August and December with 16.60±0.10 recorded as the highest at MC August (Table 1) while soil at U/Kudu recorded the lowest when compared with that of MC with 6.65±0.10 at 0 cm – 15 cm, indicating the lowest for the two months (Table 2). The results of Ca and Mg were 2.13±0.00 and 1.42±0.00 respectively at 15 cm – 30 cm which is highest at U/Kudu while 0.42±0.00 at MC and 0.28±0.00 at MC and U/Kudu were the lowest at the depth of 0 cm – 15 cm (Table 2) but when compared between the two months, the month of August recorded the highest than month of December. The results of Pb and Cu in the soil of MC were found to be higher than that of U/Kudu (Table 2). The amount of Zn and Cd were 0.64±0.00 and 0.53±0.00 respectively at the depth of 15 cm – 30 cm at MC while the lowest

were recorded at the depth of 0 cm – 15 cm in the soil of MC and U/Kudu respectively (Table 2). On the amount of Hg present in the soil of MC and U/Kudu, MC had 0.02±0.00 which is highest while both depths of U/Kudu had 0.01±0.00 including MC at 0 cm – 15 cm (Table 2), When compared between the two months it shows similar pattern of concentration (Table 1 and 2).

Table 1: Mean concentrations (mg/ kg) of Inorganic Pollutants in soils at Different Depths of MC and U/Kudu in August

	LOCATIONS				F-Value	P-Value
	Millennium City		UNGUWA Kudu			
	(0-15cm)	(15-30cm)	(0.15cm)	(15.30cm)		
pH	7.74±0.01^{d}	8.02±0.01^{b}	7.93±0.15^{c}	8.27±0.01^{a}	527.00	0.000
PO_4	3.04±0.01^{d}	9.47±0.01^{b}	5.75±0.05^{c}	10.35±0.05^{a}	9106.92	0.000
NO_3	12.05±0.05^{c}	16.60±0.10^{a}	6.70±0.10^{d}	14.60±0.10^{b}	2258.95	0.000
Ca	0.69±0.00^{d}	2.11±0.00^{b}	1.36±0.00^{c}	3.36±0.00^{a}	4633.73	0.000
Mg	0.34±0.00^{d}	1.06±0.00^{b}	0.68±0.00^{c}	1.68±0.00^{a}	8432.61	0.000
Pb	0.89±0.00^{a}	0.08±0.00^{c}	0.89±0.00^{a}	0.28±0.00^{b}	8342.64	0.000
Zn	0.13±0.00^{c}	0.44±0.00^{a}	0.27±0.00^{b}	0.27±0.00^{b}	4526.57	0.000
Cd	0.52±0.00^{a}	0.47±0.00^{b}	0.47±0.00^{b}	0.47±0.00^{b}	2552.67	0.000
Cu	0.18±0.00^{a}	0.17±0.00^{b}	0.18±0.00^{a}	0.18±0.00^{a}	7561.67	0.000
Hg	0.02±0.00^{a}	0.02±0.00^{a}	0.01±0.00^{b}	0.01±0.00^{b}	229.05	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

Table 2: Mean concentrations (mg/kg) of Inorganic Pollutants in soils at Different Depths of MC and U/Kudu in December

	LOCATIONS				F-Value	P-Value
	Millennium City		Unguwan Kudu			
	(0-15cm)	(15-30cm)	(0-15cm)	(15-30cm)		
pH	7.02±0.01^{b}	7.02±0.01^{b}	7.03±0.01^{b}	8.07±0.00^{a}	7350.44	0.000
PO4	2.03±0.01^{d}	8.16±0.01^{b}	5.32±0.01^{d}	8.80±0.10^{a}	3715.84	0.000
NO3	10.80±0.10^{c}	15.01±0.00^{a}	6.65±0.05^{d}	12.29±0.22^{b}	829.97	0.000
Ca	0.42±0.00^{d}	2.01±0.00^{b}	1.24±0.00^{c}	2.13±0.00^{a}	2840.78	0.000
Mg	0.31±0.00^{c}	1.05±0.00^{b}	0.28±0.00^{d}	1.42±0.00^{a}	8837.56	0.000
Pb	0.09±0.00^{a}	0.06±0.00^{c}	0.07±0.00^{b}	0.02±0.00^{d}	7156.74	0.000
Zn	0.13±0.00^{d}	0.64±0.00^{a}	0.21±0.00^{c}	0.37±0.00^{b}	6523.92	0.000
Cd	0.45±0.00^{c}	0.53±0.00^{a}	0.26±0.00^{d}	0.49±0.00^{b}	7623.82	0.000

Cu	0.18 ± 0.00^{c}	0.89 ± 0.00^{a}	0.18 ± 0.00^{c}	0.21 ± 0.00^{b}	6743.78	0.000
Hg	0.01 ± 0.00^{b}	0.02 ± 0.00^{a}	0.01 ± 0.00^{b}	0.01 ± 0.00^{b}	130.49	0.000

Superscripts with different letters are significantly different at $p\leq0.05$

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 pollutant 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, the pH for soil was within the limit. The result obtained for pH therefore is in consonance with the work of Ekhator *et al*., (2015).

Generally, there are certain factors that influence the levels of phosphates. These factors include location, population density, degree of agricultural and industrial activities in 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 the depth of each site soil as presented in the results. Although there is no nutritional basis for the regulation of phosphates level, it is important to control eutrophication (Nolan, 2008). All samples had PO_4 levels exceeding the maximum acceptable level.

It was found that the mean concentration of calcium was found to be within the permissible limit as reported by W.H.O (2003) for both sites and depth of soil. This therefore can help to reduce the effects on human health which include reduced bone density, increased risks of bone fracture and osteoporosis (Institute of Medicine (IOM), 1997). This result is similar to the work of Sa'eed and Abdullahi (2012) who observed that soil contain optimum concentration of Ca.

Lead is a poisonous trace element often found in polluted natural waters. It is responsible for anaemia, kidney diseases, cancer, interferes with vitamin D metabolism, affect mental development in infants and toxic to the central and peripheral nervous systems (Chika and Prince, 2020). In the present study, the amount of lead detected was higher than the permissible limit present except in the case of spinach where the amount of Lead was less than the permissible limit. The increase in the amount of lead therefore may be due to the introduction from household paint, lead batteries, fertilizers, and metal based-pesticides (Tedesse *et al*., 2018). This report is similar to the work of Aloke *et al*., (2019), Orosun *et al*., (2016) and Jagaba *et al*., (2020) where a higher amount of lead was recorded than the permissible limit.

The present study reveals the mean concentration of Zn in soil, 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 is to move hemoglobin and haemocyanin oxygen molecules in the blood (WHO, 2011). The amount of Cu present in the soil, of U/Kudu and MC were found to be within the permissible limit making it not poisonous except in spinach U/Kudu. 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.

4.0 Conclusions

The study has found out that the soil of U/Kudu and MC had adequate amount of pH and the inorganic elements are within the permissible limit of WHO and NSDWQ except PO4, Ld, Hg and Cd that were observed to be above the limit. The farmlands therefore need to be treated to reduce the concentrations to avoid the cumulative effect over time.

Recommendations

This research suggests the regular scrutiny of inorganic pollutants in soil, to avoid accrual in food chain and this elude human health risks. 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 food grown on such soil.

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Conflict of interest

All authors declare that there is no area of conflict.

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