DETERMINATION OF BIOAVAILABLE CONCENTRATIONS OF COPPER AND ZINC IN FARM SOILS IN KADUNA METROPOLIS, NIGERIA

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ABSTRACT

This study assessed the mobility and bioavailability of Cu and Zn in soils of vegetable farms located within the city of Kaduna, Nigeria vis-à-vis the soil physicochemical properties.The city was divided into 20 zones of approximately equal areas. Soil samples were taken over a period of three months from each zone for analysis of soil physicochemical properties and Cu and Zn concentrations in sequential fraction of the soil sample. Composite samples of soil were collected from vegetable farms and gardens in each zone and also from two rural villages, about 30 km south-west of the city as control. Sequential fractionation of soil samples were carried out using modified Tessier method, followed by analysis of fractions for Cu and Zn concentrations using Atomic Absorption Spectrophotometer. Mean of total concentration(μg/g) and percentage bioavailability were Cu 51.2 ±27.7 (8.1%) and Zn 238 ±89 (23.0%), respectively. Correlation analysis showed that soil pH, % organic carbon, % clay, cation exchange capacity, and metal speciation in soil influence metal mobility and bioavailability in the city soil. The mean concentrations of Cu and Zn in soil in the study site were generally higher than those of the control site, revealing some levels of pollution of the city soil by these metals. Also, the mean concentrations of Zn in some zones were significantly higher ($p < 0.05$) than established world standards such as WHO/FAO maximum permissive limit of 300μg/g in agricultural soil. The high concentrations of Zn in the soil of the vegetable farms in some zones and the high bioavailability calls for concern as this could pose a potential risk to the consumers of the vegetables grown on these farms.

Keywords: Bioavailability, Copper, Zinc, Soil, Vegetable Farms, Kaduna City, Nigeria

INTRODUCTION

The use of metals in human history has yielded great benefits as well as unexpected harmful consequences. Some metals are required in trace amounts by living organisms; some are essential for certain metabolic activities while others are essential components of enzymes and pigments in living systems (Adeniyi, 1996). Lead and cadmium, like arsenic and mercury are among the seven most toxic heavy metals, and are of no known beneficial importance in living system (Berglund *et al.*, 1984).

All toxic heavy metals can endanger human health on slight exposure; the critical organs they affect in the body differ from one metal to another (Chang *et al.*, 1992). A number of metals are said to be carcinogenic; these include arsenic, beryllium, cadmium, nickel, and hexavalent chromium (Mapanda *et al.*, 2007). Adverse health effects of lead toxicity include weariness, nausea, abdominal pain, uncoordinated body movements, inflammation of the brain tissues, IQ defects, coma and death (Fatoki, 1996).

Copper and zinc are essential metals, but are also among heavy metals that are considered environmentally important in farmed soils. High values are indicative of anthropogenic inputs, either due to excess application of fertilizers and pesticides, use of polluted water for irrigation, waste disposal, industrial and mining activities (Ashish *et al.*, 2013). Massive and regular chemical analysis of farmland soil samples could serve as a database for indicating potential micronutrient deficiency and excess or build-up, allowing preventive measures to be taken (Khan *et al.*, 2008). The complexity of metal contaminated sites has and continues to be simplified to a measure of total metal content. While total metal content is a critical measure in assessing contaminated sites, it does not provide predictive insights on the bioavailability, mobility, and fate of the metal contaminant (Maiz *et al.*, 2000). A precise evaluation of soil metal availability is necessary to assess the danger of soil contamination and to evaluate the impact of waste management practices (Mapanda *et al.*, 2007). Soil physicochemical properties such as concentration of hydrated metal oxides, organic matter content, cation exchange capacity (CEC), redox potential, pH and clay content, also have varying influence on the mobility and hence, bioavailability of metals (Mench *et al.*, 1994).

As a result of urbanization and increasing anthropogenic activities, the heavy metal pollution of soil, water and atmosphere, represents a growing environmental problem affecting food quality and human health in cities (Murphy *et al.*, 2000). Urban farming is a common practice in developing countries, including Nigeria. Kaduna, one of Nigeria's ancient cities, is highly populated and industrialized with many farms and gardens located within the city, with the majority within the vicinity of potential sources of heavy metal contaminations, such as industrial and domestic wastes, polluted water bodies and along roadsides. The aim of this study was to carry out a speciation study of copper and zinc in soil of farms and gardens within Kaduna metropolis. This was with a view to evaluate their bioavailability based on the soil physicochemical properties and the possible health implications on consumers of food crops planted on the farms.

MATERIALS AND METHODS

Sampling

The city of Kaduna was divided into 20 zones for the purpose of this study (Fig. 1). Composite samples of soil of about 0.5 kg made up of at least seven sub-samples were collected from 7 – 10 farms and gardens per zone, once in a month for a period of three months (June, July and August 2010). Samples were collected with stainless steel hand-trowel, within 0 – 20 cm depth. The sub-samples were collected along independent zigzag path to achieve randomness. The trowel was carefully cleaned after each sampling, to avoid cross-contaminations. The soil sampling spots were cleared of debris before sampling (Pouyat*et al.*, 1995). Samples were also taken from two rural villages as control (Zones 21 and 22).

Sample Preparations

Soil samples were air-dried for 7 days in the laboratory to avoid microbial degradations (Prasad, 2004). Prior to analysis, the soil samples from each zone, collected at various periods, were mixed properly and re-dried in the oven at 110°C for about 3 h and crushed in a porcelain mortar and sieved through a 2 mm plastic sieve to obtain fine soil particles (Roberts, 1999).

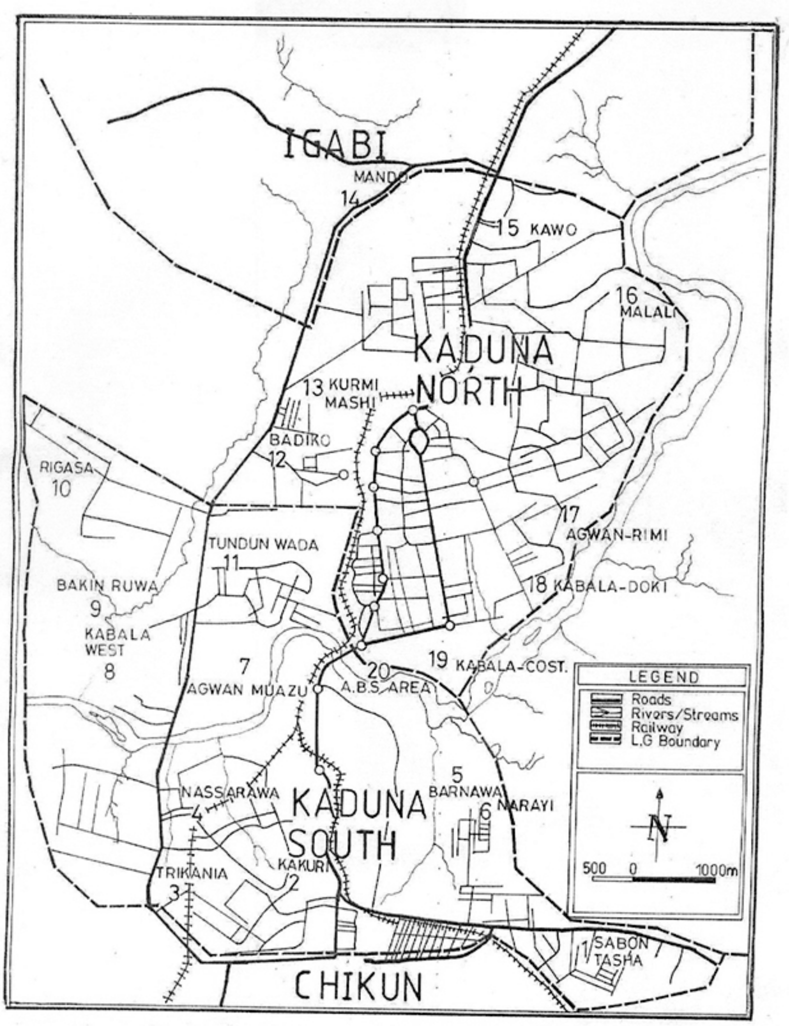

Fig.1: Kaduna Metropolis Showing the Sampling Zones

Analysis of Soil Physicochemical Properties

The most important soil physicochemical properties influencing the mobility and bioavailability of metals in soil were determined. These are soil pH (determined in water by using digital pH meter), particle size (by hydrometer method), organic matter content (by Walker-Black method) and cation exchange capacity (by Neutral KOAc saturation and Neutral NH$_4$OAc Displacement method) (Song, 2003).

Metal Speciation Studies

Metals in soil samples from each of the zones were sequentially partitioned into their different forms, using the modified Tessier Method (Vines and Rees, 1992). By this method, metals were partitioned into exchangeable (adsorbed metals), acid extractible (carbonate bound), reducible (Fe and Mn oxides bound), oxidizable (organic matter bound) and residual forms. The sequential fractionation was carried out as follows:

(i)Exchangeable Fraction

One gram of soil sample was shaken in stoppered polyethylene bottles at room temperature with 16 cm^3 of 1 M Mg(NO$_3$)$_2$ at pH 7.0 for 1 h, centrifuged and then filtered. The filtrate was made up to 50 cm^3 with distilled water and kept in polythene bottles prior to analysis.

(ii) Acid Extractable Fraction/ Carbonate Bound

To the residue from (i) above was added 25 cm^3 of 0.005M Na$_2$EDTA and shaken for 6 h, centrifuged and then filtered. The filtrate was made up to 50 cm^3 with distilled water and kept in polythene bottles prior to analysis.

(iii) Reducible Fraction/ Fe and Mn oxides Bound

To the residue from (ii) above was added 17.5 cm^3 of 0.1 M $NH_4OH.HCl$ followed by 17.5 cm^3 of 3.5 M CH_3COONH_4.The mixture was then shaken for 1h, centrifuged and then filtered. The filtrate was made up to 50 cm^3 with distilled water and kept in polythene bottles prior to analysis.

(iv) Oxidizable Fraction /Organic Matters Bound

To the residue from (iii) was added 10 cm^3 of 8.8 M H_2O_2,16 cm^3 of 0.02 M HNO_3 and 10 cm^3 of 3.5 M CH_3COONH_4 (as extracting agent). The mixture was then shaken for 5 h at 98°C, centrifuged and then filtered. The filtrate was made up to 50 cm^3 with distilled water and kept in polythene bottles prior to analysis.

(v) Residual Fraction

Mixture of HNO_3 and $HClO_4$(2:1) was added to the residue from (iv) above and heated on a hot plate for 2 h in a fume cupboard. The mixture was allowed to cool to room temperature and then filtered. The filtrate was made up to 50 cm^3 with distilled water and kept in polythene bottle prior to analysis.

After each successive extraction, the solution was centrifuged at 4500rpm for 15 min. The supernatant was removed with Whatman No. 42 filtered paper and the residue washed with distilled water followed by vigorous handshaking before the next extraction. The volume of the distilled water for rising residue was kept at a minimum.

Analysis of Fractions

Metal concentrations in fractions were determined by Flame Atomic Absorption Spectrophotometer (Perkin Elmer A-ANALYST 200), using air-acetylene flame. Instrumental calibration was carried out using five appropriate working standards for each of the metals, prepared by serial dilutions of standard stock solutions (100 ppm) produced by CPI International, USA. Blanks were also determined to ascertain the contribution of reagents to metal levels. Quality control assurance was employed by the analysis of five replicate samples of standard soil reference material (SRM 989) obtained from Wageningen Evaluation Programmes for Analytical Laboratories (WEPAL), Netherlands, using the same procedure adopted for study samples.

RESULTS AND DISCUSSION

The t-test results for the total metal concentrations (at $p \leq 0.05$) showed that statistically there existed no significant difference between certified and experimental values in the analysis of reference samples. This validated the method of analysis. Table 1 shows the physicochemical properties of soil samples. The pH values ranged between 6.5 and 7.1, while the range of % clay, % organic carbon and cation exchange capacity (CEC) are 23.8 – 38.5, 1.20 – 4.70 and 2.69 – 108, respectively. The high soil pH will decrease mobility and bioavailability of metals. Other factors such as clay content, organic matter content and cation exchange capacity (CEC) were just moderate for majority of the zones, except for Zone 15 with high CEC. Organic matter has a high sorption capacity for metals and readily form complex with them, slows the rate of hydrolysis and affects the rate and pathways of oxido-reduction reactions (Welz, 1985). High organic matter content means immobilization of the metals that bind to substances such as fulvic or humic acids. Zones with high % organic carbon, such as Zones 5, 15 and 18, are also associated with high concentrations of metals in the surface soil. This showed that metals are retained in the surface soil against the effects of leaching and plant uptake.

The results of mean concentrations (µg/g dry weight) of Cu and Zn in soil fractions are shown in Tables 2 and 3 respectively. The mean concentrations of Cu and Zn in the study site were greater than the control site, indicating some degree of pollution of the study site by these metals. Mean values revealed that Cu existed mainly in the soil samples in the order residual > reducible >oxidizable> acid extractible > exchangeable forms, while the order for Zn is residual > acid extractible > reducible >oxidizable> exchangeable forms. Table 4 compares the total metal concentrations in soil with the bioavailable concentrations. The mean total concentrations of Cu and Zn (µg/g) were 51.2± 27.7 and 238 ± 89 respectively. Mean %

bioavailability of Zn (23.0 ± 7.7%) in the study site is greater than that of the Cu (8.1 ± 5.1%), indicating that Zn is more mobile and available to the vegetables. In general, the higher the clay and/or organic matter content and pH, the more firmly bound are the metals (low mobility), and the longer is their residence time in soil, and hence, low bioavailability. Exchangeable cations are generally available to plants and microorganisms. High CEC, as found in Zone 15, could enhance metal mobility and bioavailability. However, these physicochemical factors often have a mutual effect (Welz, 1985). Table 5 shows the Pearson correlation coefficient values ($p < 0.05$) of soil properties and % bioavailability of the metals. There existed negative (inverse relation) to weak correlations between soil properties and % bioavailability. This is expected of pH, % organic carbon and % clay, as their low values are capable of enhancing bioavailability.

Table 1: Physicochemical Properties of Soil Samples

Zone	Soil Texture	% Sand	% Silt	% Clay	pH(H_2O)	OC (%)	CEC (cmol/kg)
1	Sand-Clay-Loam	58.7 ±2.1.	16.8±1.3	24.5±1.5	6.5±0.2	4.2±0.5	12.27±2.91
2	Clay-Loam	36.7±1.1	25.8±2.1	37.5±4.1	6.9±0.1	3.6±1.1	8.61±1.41
3	Sand-Clay-Loam	55.3±3.2	14.2±0.3	30.5±1.6	6.8±0.7	1.6±0.2	5.20±1.71
4	Sand-Clay-Loam	59.6±2.0	13.9±1.8	26.5±2.3	6.9±0.3	3.9±0.1	36.80±7.90
5	Sand-Clay-Loam	61.7±3.2	12.8±0.4	25.5±2.9	6.8±0.6	4.7±1.1	36.12±6.21
6	Sand-Clay-Loam	58.7±2.8	13.8±1.7	27.5±1.3	7.0±0.3	2.1±0.3	4.80±1.11
7	Sand-Clay-Loam	56.7±3.9	16.8±2.8	26.5±2.7	6.9±0.2	1.2±0.2	2.69±1.10
8	Sand-Clay-Loam	59.7±2.8	12.8±1.3	27.5±2.2	6.8±0.4	3.4±1.2	16.76±2.20
9	Sand-Clay-Loam	58.7±2.6	14.8±3.1	26.5±2.5	6.6±0.7	3.6±1.1	10.73±2.31
10	Sand-Clay-Loam	53.7±1.6	11.8±1.3	34.5±1.1	6.6±0.1	1.5±0.1	11.68±1.41
11	Sand-Clay-Loam	61.7±1.7	10.8±1.9	27.5±3.3	7.0±0.4	3.3±0.2	3.45±0.11
12	Clay-Loam	35.7±2.0	26.8±2.9	37.5±5.1	6.5±0.2	3.1±0.1	7.78±1.20
13	Sand-Clay-Loam	54.7±1.9	16.8±1.4	28.5±2.8	6.7±0.7	3.3±0.3	4.17±1.10
14	Sand-Clay-Loam	51.7±1.1	17.8±1.7	30.5±1.2	6.5±0.1	1.8±0.2	6.78±1.01
15	Sand-Clay-Loam	50.7±0.8	20.8±1.3	28.5±5.2	6.9±0.2	4.4±1.1	108.50±11.90
16	Clay-Loam	33.7±2.9	27.8±2.1	38.5±4.2	6.8±0.1	2.4±0.4	13.19±3.51
17	Sand-Clay	43.7±2.4	18.8±3.3	37.5±3.7	7.1±0.2	3.1±0.1	8.11±2.11
18	Sand-Clay-Loam	54.7±5.7	8.8±1.1	36.5±2.3	7.0±0.1	4.5±1.0	12.76±1.13
19	Sand-Clay-Loam	55.7±1.3	12.8±2.1	31.5±3.4	7.0±0.1	3.5±0.2	6.01±1.11
20	Clay-Loam	37.7±2.1	38.5±1.4	23.8±2.3	6.9±0.1	2.1±0.3	6.95±1.10
21^c	Sand-Clay-Loam	53.7±1.3	9.8±1.7	36.5±1.3	6.6±0.2	4.6±1.1	15.01±2.34
22^c	Sand-Clay-Loam	54.7±3.7	9.8±1.3	35.5±2.1	7.0±0.1	4.4±1.2	16.48±3.17

OC = organic carbon CEC = cation exchange capacity (cmol/kg) c = control

Table 2: Mean Concentrations (μg/g dry weight) of Copper in Sequentially Extracted Soil Fractions

ZONE	EXC	AEX	RED	OXD	RES	TOTAL	BA	%BA
1	0.6	2.0	11.6	3.9	22.1	40.2	2.6	6.5
2	0.4	1.9	2.8	0.4	31.8	37.3	2.3	6.0
3	0.1	1.6	4.1	3.2	13.2	22.2	1.7	7.7
4	0.4	4.8	33.2	9.6	35.6	83.6	5.2	6.2
5	0.6	6.6	37.7	15.0	74.1	134	7.1	5.3
6	0.4	0.9	7.4	2.9	18.5	30.1	1.3	4.3
7	0.1	0.8	5.2	2.5	15.9	24.5	0.9	3.7
8	2.7	10.1	6.8	12.4	30.8	62.8	12.8	20.4
9	ND	1.0	13.4	7.6	36.6	58.5	1.0	1.6
10	0.3	1.0	4.7	0.4	25.4	31.7	1.3	3.9
11	ND	1.1	2.5	2.5	14.9	21.0	1.1	5.0
12	ND	8.1	5.4	2.6	17.4	33.5	8.1	24.2
13	0.1	1.6	4.4	2.1	11.2	19.4	1.7	8.7
14	0.7	1.4	0.1	2.3	20.0	24.4	2.0	8.2
15	0.2	18.9	34.5	37.7	49.7	141	19.1	13.5
16	2.2	4.1	3.4	2.5	27.1	39.2	6.3	16.0
17	0.5	0.2	8.2	2.6	21.3	32.8	0.7	2.3
18	0.7	2.5	37.9	9.2	84.7	135	3.2	2.4
19	0.6	0.7	1.5	2.1	12.0	16.9	1.3	7.7
20	0.4	2.5	8.4	2.8	22.8	36.9	2.9	7.9
MEAN	**0.6** **±0.6**	**3.6** **±4.2**	**11.7** **±8.5**	**6.2** **±8.3**	**29.3** **±16.4**	**51.2** **±27.7**	**4.1** **±4.1**	**8.1** **±5.1**
21[c]	0.1	0.3	2.0	1.7	3.1	7.2	0.4	5.6
22[c]	0.2	0.4	3.1	2.2	10.2	16.1	0.6	3.7
MEAN	**0.2** **±0.0**	**0.4** **±0.0**	**2.6** **±0.2**	**2.0** **±0.1**	**6.7** **±1.6**	**11.7** **±2.0**	**0.5** **±0.0**	**4.7** **±0.4**

EXC = Exchangeable fraction
AEX = Acid extractable fraction
RED = Reducible fraction
OXD = Oxidizable fraction
RES = Residual fraction
BA = Bioavalable fraction = EXC + AEX
c = control

Table 3: Mean Concentrations (µg/g dry weight) of Zinc in Sequentially Extracted Soil Fractions

ZONE	EXC	AEX	RED	OXD	RES	TOTAL	BA	%BA
1	4.6	74.7	51.2	29.2	91.3	251	79.3	31.6
2	19.9	56.3	16.4	19.1	106	218	76.2	34.9
3	2.8	37.0	38.1	17.3	82.8	178	39.8	22.4
4	2.8	111	75.3	40.1	81.7	311	114	36.6
5	20.2	73.2	75.4	25.1	197	391	93.4	23.9
6	9.3	8.4	18.2	11.1	127	174	17.7	10.2
7	3.5	19.4	15.6	12.2	93.0	144	22.9	15.9
8	3.2	81.5	12.5	26.0	126	250	84.7	33.9
9	21.5	46.1	63.0	14.1	116	261	67.6	25.9
10	1.7	31.1	18.2	14.4	91.4	157	32.8	20.9
11	5.7	9.9	6.0	8.1	80.9	111	15.5	14.0
12	23.7	33.8	42.0	18.1	104	222	57.5	25.9
13	5.8	13.8	7.6	9.3	114	151	19.6	13.0
14	6.3	17.0	3.9	12.3	134	173	23.3	13.4
15	33.4	134	161	43.5	139	511	167	32.7
16	4.7	112	21.9	23.0	126	288	117	40.5
17	5.0	7.1	38.9	20.1	126	197	12.1	6.1
18	33.6	12.2	195	94.5	114	449	45.8	10.2
19	7.7	21.5	7.2	13.0	96.7	146	29.2	20.0
20	15.6	32.0	25.6	14.8	83.8	172	47.6	27.7
MEAN	**11.6** **±7.1**	**46.6** **±28.3**	**44.6** **±42.7**	**23.3** **±19.3**	**112** **±26**	**238** **±89**	**58.1** **±34.7**	**23.0** **±7.7**
21^c	2.7	6.4	19.9	11.7	44.2	84.9	9.1	10.7
22^c	1.9	3.9	10.8	9.6	35.7	61.9	5.8	9.4
MEAN	**2.3** **±0.2**	**5.2** **±0.6**	**15.4** **±2.0**	**10.7** **±0.5**	**40.0** **±1.9**	**73.4** **±5.1**	**7.5** **±0.7**	**10.1** **±0.3**

EXC = Exchangeable fraction
RED = Reducible fraction
RES = Residual fraction
c = control

AEX = Acid extractable fraction
OXD = Oxidizable fraction
BA = Bioavalable fraction = EXC + AEX

Table 4: Total and Percentage Bioavailable Concentrations (μg/g dry weight) of Metals in Soil Samples Based on Sequential Fractionation

Zone	**Cu**			**Zn**		
	Total	**BA**	**%BA**	**Total**	**BA**	**%BA**
1	40.2	2.6	6.5	251	79.3	31.6
2	37.3	2.3	6.0	218	76.2	34.9
3	22.2	1.7	7.7	178	39.8	22.4
4	83.6	5.2	6.2	311	114	36.6
6	134	7.1	5.3	391	93.4	23.9
6	30.1	1.3	4.3	174	17.7	10.2
7	24.5	0.9	3.7	144	22.9	15.9
8	62.8	12.8	20.4	250	84.7	33.9
9	58.5	1.0	1.6	261	67.6	25.9
10	31.7	1.3	3.9	157	32.8	20.9
11	21.0	1.1	5.0	111	15.5	14.0
12	33.5	8.1	24.2	222	57.5	25.9
13	19.4	1.7	8.7	151	19.6	13.0
14	24.4	2.0	8.2	173	23.3	13.4
15	141	19.1	13.5	511	167	32.7
16	39.2	6.3	16.0	288	117	40.5
17	32.8	0.7	2.3	197	12.1	6.1
18	135	3.2	2.4	449	45.8	10.2
19	16.9	1.3	7.7	146	29.2	20.0
20	36.9	2.9	7.9	172	47.6	27.7
Mean	**51.2**	**4.1**	**8.1**	**238**	**58.1**	**23.0**

BA = Bioavailability

Table 5: Pearson Correlation Coefficient of Soil Properties and % Bioavailability of Metals

	pH	**%OC**	**%Clay**	**CEC**	**%BA(Cu)**	**%BA(Zn)**
pH	1					
%OC	0.116	1				
%Clay	0.073	-0.069	1			
CEC	0.096	0.477*	-0.160	1		
%BA(Cu)	0.338	0.007	0.179	0.196	1	
%BA(Zn)	0.255	0.237	-0.059	0.384	0.508	1

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

CONCLUSION

The study showed that soils of Kaduna metropolitan vegetable farms were enriched with Cu and Zn, probably as a result of anthropogenic contributions of the metals to the environment.The concentrations of Cu and Zn in the soil samples were generally lower than WHO/FAO maximum permissive limits of 100 μg/gand 300 μg/g for Cu and Zn, respectively for agricultural soils. Furthermore, the study revealed that some areas of the city were more polluted by these metals than the other, due to the prevailing anthropogenic activities peculiar to each area. The study of the soil physicochemical properties revealed that the general high soil pH was helpful in reducing the bioavailability of the metals. The % bioavailable concentrations showed that Zn (23.0%) was more available for plant uptake than Cu (8.1%).

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