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Levels of Zinc (Zn), Copper (Cu), Iron (Fe), and Cadmium (Cd) in Soil, Rice Stalk, and *Oryza Sativa* Grain in Ishiagu Rice Field, Ebonyi State, Nigeria; Human Health Risk

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Abstract

Levels of heavy metals (Zn, Cu, Fe, Cd) were determined in soil, rice grain, and rice stalk from Federal College of Agriculture Ishiagu rice field, Ebonyi state, Nigeria. The dried samples were digested with a 1: 3 (HNO_3: HCl) mixture and analyzed with atomic absorption spectrophotometer (AAS). The mean concentration of the metals in the soil before planting, soil after harvest, and rice grain were as follows: Zn (7.28, 11.33 and24.90); Cu (3.40, 4.64 and 4.14); Fe (803.04, 735.47 and 107.78); Cd (1.14, ND and ND) and were all within FEPA and FAO/WHO limits. The daily intake values for a 60 kg adult were Zn (0.04), Cu (0.01), and Fe (0.18) and were all below the recommended limits by Codex Alimentarius standards. The Target Hazard Quotient (THQ) for Zn, Cu, and Fe was less than one (1<), and the total hazard index was less than 1, indicating that the population will not be exposed to the potential health risk from these metals. However, the metal levels should be monitored to ensure they stay at harmless levels.

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1. Introduction

Advancement and mechanization of urban growth have promoted socio-economic development in developing countries like Nigeria and the world at large. But besides all the positive effects, they cause "environmental pollution". Soil contamination by heavy metals is a significant environmental concern worldwide, as it concerns human health and food security/quality [1-5]. According to Yap *et al.* [5], the significant sources of heavy metals include anthropogenic environmental activities like mining, smelting processes, steel and iron industries, chemical industries, agriculture, and domestic activities [4]. These sources outweigh natural sources like weathering of the parent material and volcanic eruptions [5]. Recently, concern has been raised about possible contamination of the crop (rice) by heavy metals. The plants can absorb these heavy metals in the soil through

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their roots, stems, or leaves and accumulate in their organs [6, 7]. In specific concentrations, some of these heavy metals are essential to plants, but in higher concentrations can become toxic. These metals are a health hazard to living organisms due to their persistence, non-biodegradable, and non-thermal degradable environmental characteristics [5]. The uptake of metals in excessive amounts may either cause harm to the plant or enter the food chain and accumulate when these plants are taken up. Metals accumulated in the human body through the food chain cause diseases like lung cancer and damage the central nervous system, kidney, and liver [8-11].

Heavy metals, which can pose severe hazards to humans and the environment, are increasingly being found in the environment due to the growth of mining, smelting, and other industrial operations. The quality of the surrounding air, soil, and water bodies is affected by pollution from heavy metals like lead (Pb), arsenic (As), nickel (Ni), cadmium (Cd), copper (Cu), and zinc (Zn), which endangers the lives of both animals and humans through the food chain [12].

Evaluation of potential impacts on human health in contaminated environmental media is part of assessing the risk to human health [4]. Human exposure to contaminants, the type of contaminants, and the affected person's susceptibility all determine how they affect human health [4]. Health impacts may include increased risk of cancer, high blood pressure, acute neurological abnormalities in fetuses, organ dysfunction, respiratory issues, physical and mental illness, shortened life expectancy, and immune system deterioration [12].

This study is intended to determine the levels of Zinc, Copper, Iron, and Cadmium in soil, rice grain, and stalk obtained from a rice field in a local area in Nigeria (Federal College of Agriculture Ishiagu, Ebonyi state) through the determination of the physicochemical properties of the soil, evaluation of the level of contamination, and health risk assessment.

2. Experimental

2.1. Area of Study

See figure 1.

2.2. Sample Collection

The land (Federal College of Agriculture, ishiagu, rice field) is about 6 hectares, i.e. (240×75m). The land was divided into 4parts (A, B, C, and D).

2.3. Soil Sample Collection

Eight (8) composite soil samples were collected from four sections of the rice farm before plantation. Each composite is made of 5 grab samples randomly collected from each area of the rice farm. In the same way, twelve (12) composite soil samples were collected after the rice harvest. Four (4) grab samples were randomly collected from different parts of the land which has not undergone any agricultural practice (a fallow land) as the soil control. These soil samples were taken from 0-20cm depth from the surface of the ground with a clean machete, and the collected samples were placed in well-labeled polyethylene bags.

2.4. Rice Sample Collection

Twelve (12) composite rice plant samples were collected from four different sections of the farm. Each composite consists of five (5) randomly selected rice plants concerning the soil already sampled. The rice grains from each composite were separated from the stalk. The rice grains and stalks were each placed in polyethylene bags.

2.5. Sample Preparation

2.5.1. Soil Preparation

The soil samples were air-dried, crushed, and passed through a 0.16mm sieve to remove gravel-sized materials and then homogenized with a mortar and pestle. The samples were then stored in polyethylene bags with labels for analysis.

2.5.2. Rice Preparation

The rice grain samples were refined to remove the husk using mortar and pestle and winnowed with a tray pan. The polished rice grains were then stored in polyethylene bags well labeled. The rice stems were finely chopped with the knife on a wooden platform and stored in labeled polyethylene bags.

2.5.3. Ash

Two (2) ash samples were collected from 2 different abattoir sites and were mixed to get a homogenous sample. The ash was used to mix the rice seeds before broadcasting to scare birds away or prevent them from eating them.

2.5.4. Sample Size

The overall sample for analysis became: 8 for soil before planting + 12 for soil after harvest + 12 for rice grain +12 for rice stem +4 for soil control, and + 1 for ash, totaling 49 samples.

2.5.5. Digestion of Soil Samples, Rice Grain Samples, and Rice Stalk Samples

10g each of the soil and rice grain samples, 5g of the rice stalk were measured into different digestion flasks, and 40ml of Aqua-regia (Nitric acid and HCl in the ratio of 1:3) was added. The mixtures were then heated on a heating mantle to boil until the fume became clear and were allowed to cool. Each of the various digested solutions was diluted with deionized water and filtered through a filter paper into 100ml volumetric flasks and were made up to the mark with deionized water. The solutions were finally kept in test tubes. Concentrations of Zn, Cu, Fe, and Cd were determined using the AA-7000 atomic spectroscopy. Statistical analysis of the data obtained was done using SPSS version 17 for windows and Palisade analysis.

2.6. Quality Assurance

The precision of the analytical procedure was investigated by carrying out recovery experiments. This was done by determining the metals' concentration in duplicate spiked and unspiked rice samples. Spiking was done by adding 1 ML of 2ppm and

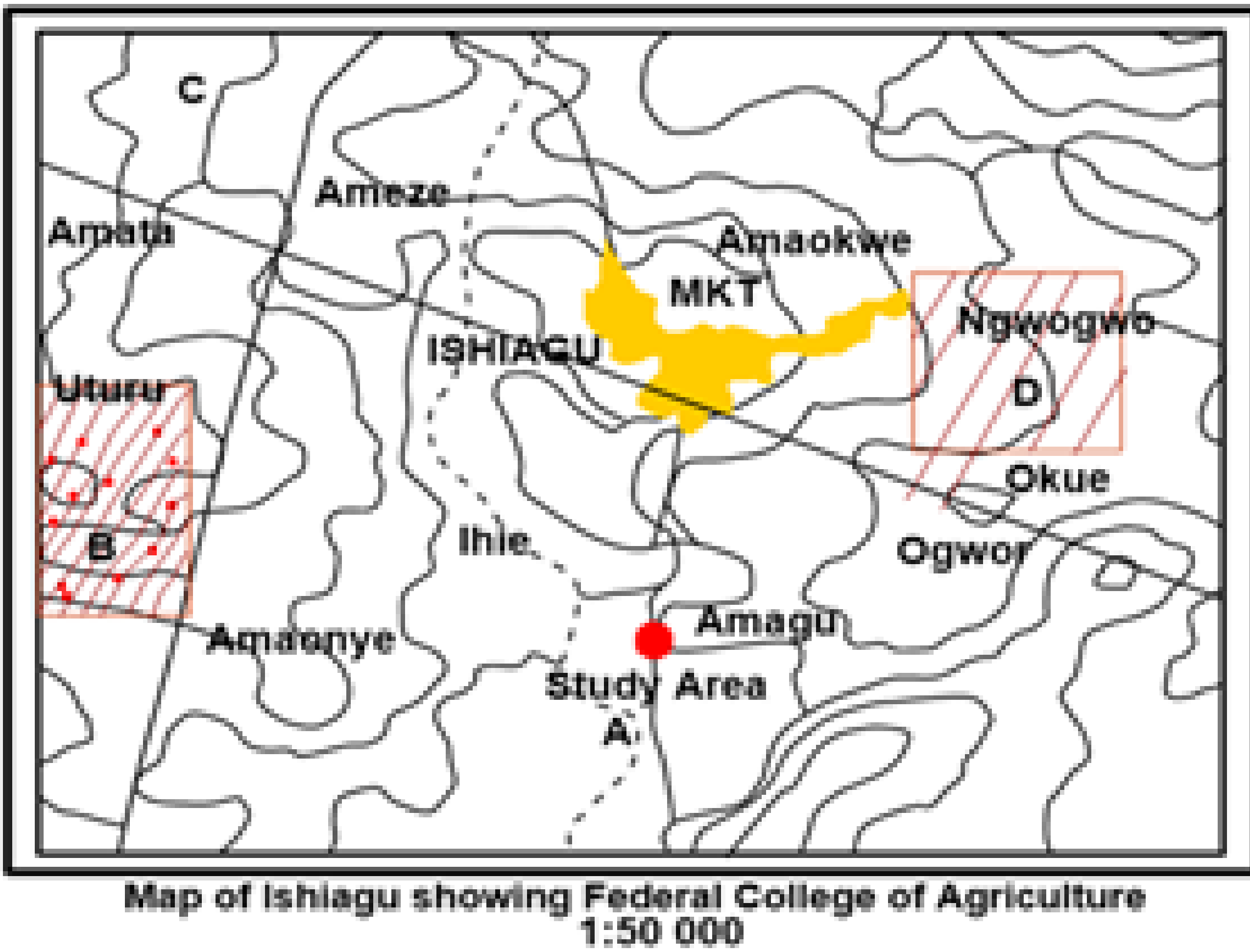

Figure 1. Area of study

4ppm metal solution to 2 g of samples, which were later subjected to the digestion procedure.

$$\%\ recovery = \frac{a - b\ \times 100}{c}, \tag{1}$$

where a denotes concentration in the spiked sample, b represents concentration in the unspiked sample and c denotes concentration of the metal ion added.

2.6.1. Risk Assessment

This process evaluates the potential effects of a contaminant on humans from doses received through one or more exposure pathways. The health risk from rice consumption was assessed using the target hazard quotient (THQ) and total hazard index (THI) [13]. The target hazard quotient (THQ) is the ratio of the determined dose of a pollutant to a reference dose level. In contrast, the total hazard index (THI) evaluates the potential risk of adverse health effects from a mixture of chemical constituents in rice. If this ratio is less than 1, the exposed population is unlikely to experience noticeable adverse effects [14-16].
The following equation calculated the THQ and THI values for the metals:

$$THQ = \frac{EF \times ED \times IR \times C}{RfD \times BW \times AT} \times 10^{-3} \tag{2}$$

$$THI = \quad T\ \ HQ_1 + THQ_2 + \cdots + THQ_n \tag{3}$$

Where THQ is the target hazard quotient, EF is the exposure frequency (365 days /year), ED is the exposure duration (54 years), IR is the rice ingestion(kg/person/day), and C is the metal concentration in rice (mg/kg), RFD is the oral reference dose (mg/kg/day) and AT is the average time for non–carcinogens (365 days /year× ED). The oral reference dose for metals
(mg/kg/day) were: Cu(0.040), Zn(0.300), Fe(0.700) [17]. The calculated THQ value is also shown in Table 2. It is less than 1, thus indicating that the Nigerian population has not been exposed to the potential health risk of dietary copper via rice consumption.

2.7. Data Analysis

Data obtained were analyzed with SPSS 17 for windows. Correlation coefficient analysis was carried out to establish the correlation pattern of various metal pairs in soil and rice grain samples. The student's t-test was carried out to determine any significant difference in the metal concentration in the soil before planting and after harvest at $p<0.05$.

3. Results and Discussion

Table 1 shows recoveries ranging from 84% to 128% with a mean of 96% and precision of 5.7, a value lower than 10% indicating high accuracy.

3.1. Heavy Metals Concentration in Soil and Rice Grain

3.1.1. Copper in Soil

The concentrations of Copper (Table 2) in the soil samples from the control portion ranged from 1.67 mg/kg - 3.33 mg/kg. The lowest value (1.67 mg/kg) was recorded at $Control_{2,}$ while the highest (3.33 mg/kg) was at $Control_4$. These concentrations gave a mean ± SD of 2.22 ± 0 .75 (Table 3).
As in Table 2, the concentration of copper in the "soil before planting" ranged between 2.39 mg/kg - 5.18 mg/kg. The lowest value (2.39 mg/kg) was recorded at D_2 and the highest (5.18 mg/kg) at $A_{1.}$ These gave a Mean ± SD of 3.40 ± 0.91 (Table 3). Also, the concentrations of copper (Table 2) in "soil after harvest" ranged from 3.70 mg/kg to 6.07mg/kg. A_3 had the lowest value (3.70mg/kg), and B_2 had the highest value (6.07 mg/kg). The mean ± SD was 4.64 ± 0.69 (Table 3).
It compared the mean concentrations of ("soil before planting" and "soil after harvest") (3.40 mg/kg and 4.64 mg/kg, respectively) with the mean concentration of the "soil control" (2.22 mg/kg). It can be seen that the soil was slightly contaminated with copper. This contamination could be attributed to the use of pesticides or herbicides. This possibility was supported by the fact that most pesticides used in agricultural soils were based on compounds containing Cu, Hg, Mn, Pb, or Zn [18].
The results compared with other researchers; Zhuang reported 502 mg/kg as the mean concentration of copper in agricultural soils around the Daboshan mine in Guandong, China. Also, Song recorded 8.41-148.73 mg/kg as the mean concentration of copper in agricultural soils of Suxian County, South China. This variation of results might be due to the copper concentrations in irrigation water and other agronomic practices in the respective areas [16, 19]. However, the mean concentrations of Cu in (soil before planting (3.40) and soil after harvest (4.64) is below the permissible limits;

1. 150 mg/kg as with Chinese Environmental Quality Standards (1995) for soils [9].
2. (70-80) mg/kg as with FEPA (1991) guidelines for heavy metals in soil. The low concentrations recorded in this study may be attributed to the continuous removal of copper by rice grown in the field. Therefore, the concentration of Copper in Soil may not harm mice and humans when used for rice production [3].

3.1.2. Copper in Rice

The concentration of copper in "Rice stalk" as in Table 2 above ranged between 0.74mg/kg-11.06mg/kg with A_1& B_3 having the lowest value (0.74 mg/kg) and A_3having the highest value(11.06mg/kg).
These concentrations gave a mean ± SD of 2.46 ± 2.95, as in Table 3.
As in Table 2 above, the concentration of copper in "rice grain" ranged between 1.84mg/kg-14.81mg/kg, with A_2 having the lowest value (1.84 mg/kg) and C_3 having the highest value (14.81 mg/kg). The concentrations gave a mean ± SD value of 4.14 ± 3.92as seen in Table 3.
In Tanzania, Machiwa reported the mean concentration of Cu in rice collected from different locations to be 3.7mg/kg. Also, in Guandong, China, Zhuang reported the mean concentration of Copper in Rice as 6.34 mg/kg [16, 20]. However, the mean Cu concentrations of the rice samples in this study are within China's maximum permissible limits (10 mg/kg) [21]. They are also within the FAO/WHO recommended limits (20 mg/kg) for copper in rice grains, which means that the rice is suitable for consumption [21].

3.1.3. Relationships Between Copper Concentration in the Soil Before Planting and Soil After Harvest

Statistical analysis with student T-test indicates a significant difference in the metal (Copper) concentration of the soil before planting and after harvest at $p=0.05$ with a calculated value of 3.27. Table 3 shows the results of the student T-test for metal concentrations in the "soil before planting and soil after harvest."

3.1.4. Zinc in Soil

The Zinc concentration in the soil samples collected from the "control portion" as in Table 2 ranged between 3.73 mg/kg - 8.43 mg/kg. The lowest value (3.73 mg/kg) was recorded in $control_{2,}$ while the highest (8.43 mg/kg) was in $control_2$. These concentrations gave a mean ± SD of 5.26 ± 2.2, as shown in Table 3. Also, the concentration of Zinc in the "soil before planting" (Table 2) ranged between 2.75mg/kg - 13.17mg/kg with the lowest value (2.75mg/kg) at A_1 and the highest value (13.17mg/kg) at A_2. These gave a mean ± SD of 7.28 ± 3.90 (Table 3).
As in Table 2, the Zinc concentration in "soil after harvest" ranged between 6.88mg/kg-15.15mg/kg. The lowest value was C_3(6.88 mg/kg), while the highest was D_3(15.15 mg/kg). The mean ± SD is 11.33 ± 2.51, as in Table 3. Comparing the mean concentration of zinc in the "soil before planting and soil after harvest" (7.28 mg/kg and 11.33 mg/kg respectively) with that of the soil control (5.26 mg/kg) as seen in Table 2, It can be seen that their values are more than that in the "soil control" suggesting that the soil is contaminated with zinc. The contamination could be attributed to pesticides and herbicides on the field, as zinc is one of the constituents of most pesticides [18].
Also, we compared the results with those reported by researchers like;

1. Zhuang reported that the Zn concentrations of the agricultural soils around the Daboshan mine in Guangdong,

China is 498 mg/kg [14].

2. Machiwa reported the mean zinc concentration as 65.46mg/kg in the agricultural soils of Lake Victoria basin, Tanzania [20].

3. Kibassa reported the average range concentration of zinc in agricultural soils collected from six sites in Daressalan to be 33.18 mg/kg [22].

The mean concentrations gotten from the different soil portions (soil before planting and soil after harvest, 7.28 mg/kg and 11.33 mg/kg, respectively) in this study did not exceed that recorded by the researchers mentioned earlier and also are far below the maximum permissible limits (300-400 mg/kg) for zinc in soils by (FEPA) and (300 mg/kg) as with Grade ii Environmental Quality standards for agricultural soils in China. Therefore, the soil may not be harmful to rice production for consumption by human beings.

3.1.5. Zinc in Rice

The concentration of zinc in "Rice stalks" (Table 2) ranged between 15.14 mg/kg and 69.03 mg/kg, with D_2 having the lowest value (15.14 mg/kg) and A_1 having the highest value (69.03mg/kg). These concentrations gave a mean ± SD of 45.14 ± 13.73, as shown in Table 3. Also, the concentration of zinc in "rice grain" ranged between 14.78 mg/kg-32.89mg/kg, as shown in Table 2, with D_1 having the lowest value (14.78 mg/kg) and B_2 has the highest value (32.89 mg/kg). The mean ± SD value was 24.90 ± 6.06, as shown in Table 3.

It compared the mean concentration of zinc in rice grains (24.90 mg/kg) in this study with those reported by [20] (21.7 ug/g) and that reported by [23] (21.5 ug/g). It was found that they are still within the range, although most of the concentrations of zinc in rice individually in this study fall within these limits except for a few which are a bit higher in the rice grains in areas A_2, B_2, B_3, and C_1(31.37,32.89,30.81, and 29.48 mg/kg respectively). The concentrations in the rice stalk were relatively high. This could be attributed to the ash from the abattoir (rubber tire), which was used to mix the rice grains before broadcasting on the field to avoid /scare birds from eating the broadcasted rice. This ash contains zinc, which was made highly available to the rice stalk then, followed by the little the rice grain absorbed. However, the mean concentrations are still within the Chinese maximum permissible limits for zinc in rice (50 mg/kg) and the FAO/WHO (2002) recommended limits for zinc in rice grains. Therefore, rice is suitable for consumption [17].

3.1.6. Relationships Between Zinc Concentrations in the Soil Before Planting and Soil After Harvest

The statistical analysis with the student T-test indicated a significant difference in the soil's metal (Zinc) concentration before and after planting at p=0.05 with a calculated value of 2.60. Table 3 shows the results of the student T-test for metal concentration in the soil before and after planting.

3.1.7. Iron in Soil

The concentration of iron in "soil control" ranged between 805.26 mg/kg - 823.69 mg/kg, as shown in Table 2, with $control_1$ having the lowest value (805.26) and $control_4$having the highest value (823.69 mg/kg) and a Mean ± SD of 814.40 ± 7.52 as in Table 3.

As in Table 2, the iron concentrations in the "soil before planting" ranged between 764.29 mg/kg - 845.59 mg/kg. D_2 had the lowest value (764.29 mg/kg) while A_1 had the highest value (845.59mg/kg), and the Mean ± SD value was 803.04 ± 26 as in Table 3.

Also, the iron concentrations in "soil after harvest" ranged between 611.14-838.81 mg/kg, as in Table 2. The lowest value (611.14 mg/kg) was recorded at C_2 and the highest (838.81 mg/kg) at D_2. The Mean ± SD value was 735.4 ± 73.20, as shown in Table 3. Comparing the mean concentration of iron in (soil before planting and soil after planting) (803.04 mg/kg and 735.47 mg/kg, respectively) with soil control (814.40mg/kg). These values are lower than the soil control value meaning the soil is not contaminated with iron. However, the mean concentrations in soils (before planting (803.04mg/kg) and after harvest (735.47 mg/kg) are still within the maximum permissible limits (7000-550000) as with Chine's grade ii Environmental quality standards [24].

3.1.8. Iron in Rice

The iron concentrations in "Rice stalk" ranged between 56.61mg/kg-300.12mg/kg, as shown in Table 2. The lowest value (56.61 mg/kg) was recorded at C_2, and the highest 300.12 mg/kg value was recorded at B_2. The Mean ± SD value was 150.02 ± 85.20as shown in Table 3.

The iron concentrations in "rice grain," as shown in Table 2, ranged between 0.66mg/kg-392 mg/kg. The lowest value (0.66 mg/kg) was recorded at B_3 and the highest value (392.35 mg/kg) at D_2. The Mean ± SD value was 107.78 ± 138.15, as in Table 3.

3.1.9. Relationships Between the Iron Concentration in the Soil (Before Planting) and Soil (After Harvest)

The statistical analysis with the student T-test indicated a significant difference in the soil's metal (Iron) concentration before and after planting at p=0.05 with a calculated value of 2.92. Table 3 shows the results of the student T-test for Metal concentrations in the soil before and after planting.

3.1.10. Cadmium in Soil

Cadmium concentrations were detected in only one portion; in the "soil before planting" area A_1, with a value (1.14 mg/kg), as shown in Table 2.

3.1.11. Cadmium in Rice

The concentrations of Cadmium in "rice stalk" were scantily detected at A_1, B_1, B_2, C_3 & D_1 with the range (0.02mg/kg-2.03mg/kg) as shown in Table 2. The lowest value (0.02 mg/kg) was recorded at B_2 and the highest value at D_1. The mean ±SD was 0.53±0.85, as shown in Table 3. The mean cadmium concentration in rice stalk was higher than the Codex standards (1993-1995) (0.1mg/kg) for Cadmium in Rice stalk. This high value could be attributed to the ash (from the abattoir (rubber tire) that was used to mix the rice seeds before broadcasting on the rice field [25]. However, none of these concentrations were made available to the rice grain, which leaves the conclusion that the rice grain is free from Cadmium contamination and is, therefore, fit for consumption.

3.1.12. Zinc Concentrations in Soil

Zinc concentration in the "soil before planting" ranged between 2.75mg/kg and 13.17, with a mean of 7.28. Zinc concentration in "soil after harvest" ranged between 6.88mg/kg and 15.15 mg/kg, with a mean of 11.33. The mean concentrations of zinc from the different soil portions (soil before planting and soil after harvest) in this study are below the 33.18 mg/kg and 65.46 mg/kg reported by kibassa and Machiwa as average range concentration of zinc in agricultural soils of Daressalan and lake victoria basin, Tanzania respectively [20, 22]. Moreover, the mean zinc concentration in the soil did not exceed the maximum permissible limits (300-400 mg/kg) for zinc in soils by FEPA and (300 mg/kg) as with Grade ii Environmental Quality standards for agricultural soils in China [24].

3.1.13. Copper Concentration in Soil

Copper concentration in "soil before planting" ranged between 2.39mg/kg and 5.18 mg/kg, with a mean of 3.40. The Concentrat**ions** of copper in the soil after harvest ranged between 3.70 mg/kg and 6.07 mg/kg, with a mean of 4.64. These mean concentrations are below the permissible limits of 150 mg/kg as with Chinese Environmental quality standards for soil and 70-80 mg/kg as with EPA guidelines for heavy metals in soil. The low concentrations are in line with 8.41-148.73mg/kg as reported by Song as the mean concentration of copper in agricultural soils of Suxian County, South China [19].

3.1.14. Iron Concentration in Soil

Iron concentration in "soil before planting" ranged between 764.29 mg/kg and 845.59 mg/kg, with a mean of 803.04. Iron concentrations in "soil after harvest" ranged between 611.14 and 838.81 mg/kg with a mean of 735.4. However, the mean concentrations are still within the maximum permissible limits (7000-550000) as with Chinese grade ii Environmental quality standards [24].

3.1.15. Heavy Metals in Rice Grain

Zinc in Rice Grain

Zinc concentration in rice grain ranged between 14.78 mg/kg and 32.89 mg/kg, with a mean of 24.90. This mean value is within the 21.5g/g reported by Herawati and the 21.7g/g reported by Machiwa as the mean concentration of zinc in rice collected from different locations in Tanzania [23, 20]. However, the zinc mean concentration in this study is below the 50mg/kg recommended limits by FAO/WHO (2002) for zinc in rice grains. Hence it is worth noting that the rice may not pose any kind of danger to human health as a result of Zinc contamination [26].

Copper in Rice Grain

The concentration of copper in rice grain ranged between 1.84 mg/kg-14.81mg/kg with a mean of 4.14. This mean value is not far from the 3.7 mg/kg reported as a copper concentration in rice grain collected from different locations In Tanzania by Machiwa and the 6.34 mg/kg reported as the mean concentration of copper in rice from Guangdong, China, by Zhuang [16]. However, the mean Copper concentration of the rice grain samples in this study is within the maximum permissible limits,10 mg/kg by China and 20 mg/kg by FAO/WHO (2002), which shows that the rice is good for consumption. [20, 14].

Iron in Rice Grain

Iron concentrations in "rice grain" ranged from 0.66mg/kg-392mg/kg with a mean of 107.78.

Cadmium in Rice Grain

Cadmium was not detected in "rice grain" for all the rice grain samples.

Correlation Matrix

Correlation is a statistical technique that shows whether and how strongly pairs of variables are related. Table 4 presents the correlation matrix for the metals in the soil before planting. A strong positive and significant correlation was observed between copper and iron with an R-value of 0.787. The strong positive correlation suggests the similar origin of the metal pairs, probably from agrochemicals used on the farm. Liu reported strong correlations among Cu, Ni, and Cr in the soil around an electroplating plant and have implied that the metals have the same pollution sources [27, 28]. A weak positive correlation was observed between zinc and iron (r=0.345). However, a weak negative correlation (r=-0.030) was observed between copper and zinc, showing that an increase in the concentration of one metal results in a decrease in the concentration.

Table 5 presents the correlation matrix for the metals in the soil after harvest. Weak positive correlations were observed between Cu-Fe, Cu-Zn, and Fe-Zn pairs. Table 6 presents the correlation matrix for the metals in the rice grain. A weak positive correlation was observed between Cu-Zn, showing that an increase in the concentration of one metal results in a decrease in the concentration of another.

3.1.16. Dietary Intake of Heavy Metals and Potential Health Risks Via Rice Consumption

Table 7 shows the metal concentrations (mg/kg) in rice, provisional maximum tolerable daily intake (PMTDI) (mg/kg BW) with estimated daily intake (EDI)(mg/kg BW/day), and target hazard quotient (THQ) data for a 60 kg adult. The intake of heavy metals was estimated by multiplication of daily consumption rate with metal content in rice divided by the bodyweight

$$EDI = \frac{M_{C} \times IR}{BW} \quad (4)$$

Where; M_c= Concentration of the heavy metal in contaminated rice, IR= ingestion rate or average rice consumption in the study region, and BW= Bodyweight.

Table 1: Recoveries and precision (%) of metals Cu, Zn, Fe, and Cd from spiked soil, ash, rice grain, and stalk samples after digestion

Element	Sample	Spike (g/mL)	Conc in unspiked sample (g/mL)	Conc in spiked sample (g/mL)	Recovered conc. (g/m L)	Recovery (%)	Precision
ZINC	Soil before planting A	2ppm	2.000	3.8182	1.8182	92	6.3
		4ppm	2.000	5.9827	3.9827	100	
	Soil before planting B	2ppm	0.2251	1.9134	1.6883	84	4.1
		4ppm	0.2251	3.8009	3.5758	89	
	Control 1	2ppm	0.3723	2.1126	1.7403	87	2.5
		4ppm	0.3723	3.9307	3.5584	89	
	Control 2	2ppm	0.2078	2.1039	1.8961	95	0
		4ppm	0.2078	4.0260	3.8182	95	
	Ash	2ppm	5.3506	7.4632	2.1126	106	4.8
		4ppm	5.3506	9.2987	3.9481	99	
	Soil after harvest A	2ppm	0.7100	2.4242	1.7142	86	8.5
		4ppm	0.7100	4.5801	3.8701	97	
	Soil after harvest B	2ppm	0.6494	2.4242	1.7748	89	4.6
		4ppm	0.6494	4.4675	3.8181	95	
	Grain 1	2ppm	0.9524	2.7965	1.8441	92	1.1
		4ppm	0.9524	4.6667	3.7143	93	
	Grain 2	2ppm	0.7013	2.5108	1.8095	90	5.3
		4ppm	0.7013	4.5628	3.8615	97	
	Stalk 1	2ppm	2.6753	4.4242	1.7489	87	3.5
		4ppm	2.6753	6.554	3.8787	97	
	Stalk 2	2ppm	1.7489	3.6190	1.8701	94	2.3
		4ppm	1.7489	5.6190	3.8701	97	
IRON	Soil before planting A	2ppm	111.2664	113.4672	2.2008	110	4.7
		4ppm	111.2664	115.4236	4.1572	103	
	Soil before planting B	2ppm	128.2620	129.9738	1.7118	86	14.3
		4ppm	128.2620	132.5546	4.524	113	
	Control 1	2ppm	132.7860	134.2533	1.4673	72	33.9
		4ppm	132.7860	137.5546	4..7686	119	
	Control 2	2ppm	128.5066	131.0742	2.5676	128	27.8
		4ppm	128.5066	131.9301	3.4235	86	
	Ash	2ppm	106.8646	108.5764	1.7118	86	0
		4ppm	106.8646	110.2882	3.4236	86	
	Soil after harvest A	2ppm	134.7424	136.8210	2.0786	104	6.4
		4ppm	134.7424	138.5328	3.7904	95	
	Soil after harvest B	2ppm	132.4192	134.1310	1.7118	86	4.7
		4ppm	132.4192	136.0873	3.6681	92	
	Grain 1	2ppm	1.9563	3.6681	1.7118	86	11.3
		4ppm	1.9563	5.9913	4.035	101	
	Grain 2	2ppm	1.2227	3.1790	1.9563	99	5.5
		4ppm	1.2227	5.5022	4.2795	107	
	Stalk 1	2ppm	6.6026	8.6812	2.0786	104	4.2
		4ppm	6.6026	10.5153	3.9127	98	
	Stalk 2	2ppm	10.0262	11.9825	1.9563	99	1.4
		4ppm	10.0262	14.0611	4.0349	101	
COPPER	Soil before Planting A	2ppm	0.0323	2.0693	2.037	102	1.4
		4ppm	0.0323	4.0416	4.0093	100	
	Soil before planting B	2ppm	0.0000	1.9723	1.9723	99	0
		4ppm	0.0000	3.9769	3.9769	99	

Control 1	2ppm	0.0000	1.8430	1.8430	92	5.2
	4ppm	0.0000	3.9769	3.9769	99	
Control 2	2ppm	0.0647	1.9400	1.8753	94	1.1
	4ppm	0.0647	3.8799	3.8152	95	
Ash	2ppm	5.2702	7.3395	2.0693	103	2.8
	4ppm	5.2702	9.2148	3.9446	99	
Soil after harvest	2ppm	0.2587	2.0370	1.7783	89	1.1
A	4ppm	0.2587	3.8476	3.5889	90	
Soil after harvest	2ppm	0.2587	2.2633	2.0046	100	3.7
B	4ppm	0.2587	4.0739	3.8152	95	
Grain 1	2ppm	0.0000	1.7460	1.7460	87	12.5
	4ppm	0.0000	4.1709	4.1709	104	
Grain 2	2ppm	0.0647	2.0693	2.0046	100	2.2
	4ppm	0.0647	3.9446	3.8799	97	
Stalk 1	2ppm	0.0647	1.9400	1.8753	94	1.1
	4ppm	0.0647	3.8476	3.7829	95	
Stalk 2	2ppm	0.0970	1.8753	1.7783	89	1.6
	4ppm	0.0970	3.7182	3.6212	91	
						X=5.7
					X=96	

Table 2: Metals concentrations (mg/kg)

Sample	Copper	Zinc	Iron	Cadmium
Soil control 1	1.85	3.81	814.32	-
2	1.67	3.73	814.31	-
3	2.04	5.06	805.26	-
4	3.33	8.43	823.69	-
Soil before planting				
A_1	5.18	2.75	845.59	1.14
A_2	4.05	13.17	821..89	-
B_1	3.32	9.11	812.46	-
B_2	3.30	7.48	803.78	-
C_1	3.68	6.98	785.79	-
C_2	2.59	3.99	774.81	-
D_1	2.68	11.68	815.74	-
D_2	2.39	3.09	764.29	-
Ash 1	156.81	42.07	848.28	-
Soil after harvest				
A_1	5.55	13.74	789.75	3-.68
A_2	4.25	12.51	761.50	-
A_3	3.70	12.16	761.35	-
B_1	4.25	9.49	746.86	-
B_2	6.07	9.00	759.38	-
B_3	4.04	8.29	736.97	-
C_1	4.25	10.21	703.58	-
C_2	4.26	12.96	611.14	-
C_3	4.60	6.88	659.74	-
D_1	5.32	13.11	625.99	-
D_2	4.80	12.41	838.81	-
D_3	4.59	15.15	830.55	-
Rice stalk				
A_1	0.74	69.03	61.86	0.20
A_2	5.15	46.61	86.51	-
A_3	11.06	58.33	144.68	-

B_1	1.48	33.16	280.15	0.16
B_2	1.85	39.05	300.12	0.02
B_3	0.74	41.26	185.20	-
C_1	1.48	46.10	197.25	-
C_2	1.85	41.01	56.61	-
C_3	1.11	41.74	60.60	0.22
D_1	1.47	51.36	126.97	2.03
D_2	1.11	15.44	213.29	-
D_3	1.48	58.62	86.95	-
Rice grain				
A_1	2.03	23.06	15.13	-
A_2	1.84	31.37	10.49	-
A_3	2.03	28.46	61.16	-
B_1	1.85	19.88	2.63	-
B_2	2.03	32.89	213.71	-
B_3	2.04	30.81	0.66	-
C_1	7.92	29.48	22.92	-
C_2	8.86	24.62	16.42	-
C_3	14.81	23.78	22.37	-
D_1	2.21	14.78	289.63	-
D_2	2.04	24.59	392.35	-
D_3	2.03	15.07	245.83	-

Table 3. Mean ± SD of metal concentrations (mg/kg)

Sample	Copper	Zinc	Iron	Cadmium
Soil control	2.22 ± 0.75	5.26 ± 2.2	814.40 ± 7.52	-
Soil b/4 planting	3.40 ± 0.91	7.28 ± 3.90	803.04 ± 26.76	1.14
Ash	156.81 ± 156.81	42.07 ± 42.07	848.28 ±848.28	-
Soil after harvest	4.64 ± 0.69	11.33 ± 2.51	735.47 ± 73.20	-
Rice stalk	2.46 ± 2.95	45.14 ± 13.73	150.02 ± 85.20	0.53±0.85
Rice grain	4.14 ± 3.92	24.90 ± 6.06	107.78 ± 138.15	-

Table 4. Pearson's correlations between different metals in the soil before planting

	Cu	Zn	Fe
Cu	1		
Zn	-0.030	1	-
Fe	0.787	0.345	1

Table 5. Pearson's correlations between different metals in the soil after harvest

	Cu	Zn	Fe
Cu	1	-	-
Zn	0.071	1	-
Fe	0.079	0.274	1

Table 6. Pearson's correlations between different metals in rice grain

	Cu	Zn	Fe
Cu	1	-	-
Zn	0.031	1	-
Fe	-0.338	-0.373	1

Table 7. Metal concentrations (mg/kg) in rice, PMTDI (mg/kg /person/day) with EDI (mg/kg bw/day) and THQ data for a 60 kgadult

METAL	MEAN ± SD	PMTDI	EDI	THQ
Copper	4.14±3.92	0.05-0.5	0.01	0.00017
Zinc	24.90±6.06	0.3-1	0.04	0.00014
Iron	107.78±138.15	0.8	0.18	0.00026
Cadmium	-		-	-

Provisional maximum tolerable daily intake (PMTDI) by JECFA

According to the international rice research institute (2001), the average Nigerian consumes 24.8kg of rice per year, equivalent to 0.1kg per person/day. The daily intakes for a 60 kg adult were compared to the provisional maximum tolerable daily intakes as stipulated by Joint FAO/WHO Expert Committee Food Additive (JECFA). It was found that the EDIS of the metals falls within the range of the safe values stipulated by JECFA [29]. The target hazard quotient (THQ) of heavy metals from rice consumption is in decreasing order: Fe>Cu>Zn and are all less than 1 indicating there will be no health risk. The total hazard index (THI) for rice consumption for a 60-kg adult is 0.00057, which is less than 1. Thus, the consumption of rice from this field will show no adverse effects from the metals.

4. Conclusion

This research demonstrated that Zn, Cu, and Fe concentrations in soil and rice grains did not exceed the threshold set by several international organizations. The preliminary maximum tolerated daily intake (PMTDI) established by JECFA was less than the metals' estimated daily intake (EDI). The total hazard index was also less than one, indicating no potential health risk associated with the intake of rice in this field. The metal's target hazard quotient (THQ) was less than one. The result from the physicochemical analysis of the soil showed that the soil is a type suitable for rice production.

However, we recommend that the field be monitored continuously to ensure that the metals stay at harmless levels.

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