

Levels and Health Risk Assessment of Heavy Metal Contamination in Soil and Different Varieties of Rice from Jere Agricultural Locations, Borno State, Northeastern Nigeria

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ARTICLE INFO

Article history:

Received
Received in revised form
Accepted
Available online

Keywords:

Heavy Metals
Soil, Rice
Potential Ecological Risk Index
Health Risk Assessment

ABSTRACT

The present study was conducted to evaluate the levels, ecological and health risk of some heavy metals which include Hg, As, Pb, Cd, Ni and Cr from agricultural soils in Maiduguri Metropolis agricultural Location, North East Nigeria. The levels of the studied heavy metals were determined using Atomic Absorption Spectroscopy (AAS). The concentrations of the studied metals in the soil samples were significantly higher at a depth of 0-5 cm, while 10-15 cm showed the lowest. The concentrations of all the metal in the soil from both locations were relatively lower than the WHO/FAO permissible limits, while that of rice were all above the said WHO/FAO limits. Results from potential ecological risks assessment and potential ecological risk index (RI) indicate low ecological risk, except Cd. Also, AEI results for all the metals were greater than 1, indicating a possibility of likelihood to induce adverse biological effects to benthic organism with exception to Hg and Cd. The geo-accumulation index, contamination factor and pollution load index were observed to be low contamination and polluted for all the heavy metal except for Pb (Igeo) and Hg (CF). The soil ADD values for children and adult via ingestion and dermal contact were lower than their individual RfDs, which shows no threat from non-carcinogenic risk as a result of metal contamination. Inhalation routes for children and adult were higher than the RfDs values, indicating human health risk. The HQ and HI via ingestion and dermal pathways were lower than the threshold values, with exception of HQ and HI inhalation for both locations were much greater than 1, an indication of high potential non-cancer related illness. For all the varieties of rice, the HQ and HI values for all the metals were less than the US EPA permissible safety limit of 1, and therefore does not pose any serious health risk concern, except As which is greater than one (1), indicating high potential non-cancer health risk via consumption of rice. Carcinogenic health risk values of As, Pb and As in the soil via inhalation pathway for children and adult with ranged of 2.23×10^{-3} to 8.10×10^{-1} were higher than the said regulatory acceptable values of 1.0×10^{-6} to 1.0×10^{-4} showing possibility of inducing cancer risk, though CR_{ing} and CR_{dermal} contact values for children and adult were within safety limits. Also, the potential health risk for children via the exposure pathways was greater than for adults, with exception of inhalation. Hence, the main exposure pathway of heavy metals for both children and adults is inhalation, followed by ingestion and dermal contact. Findings from this study suggest that values of some metals were high enough to cause health risk to human. The study further recommends regular monitoring of heavy metal in the soil and varieties of rice within the study locations in order to protect human health.

1. Introduction

Rice (*Oryza sativa*) is one of the most cereal crops cultivated worldwide and is consumed globally in Africa. In Asia countries, rice account for about 50-80% of daily caloric in-take. In Africa, rice serves as an important food

crop with a yield of about 5082 kg ha^{-1} [1]. In Nigeria in the country as they all provide favourable to support the cultivation of food crops. FARO is the acronym for Federal Agricultural research *Oryza* in Nigeria. FARO

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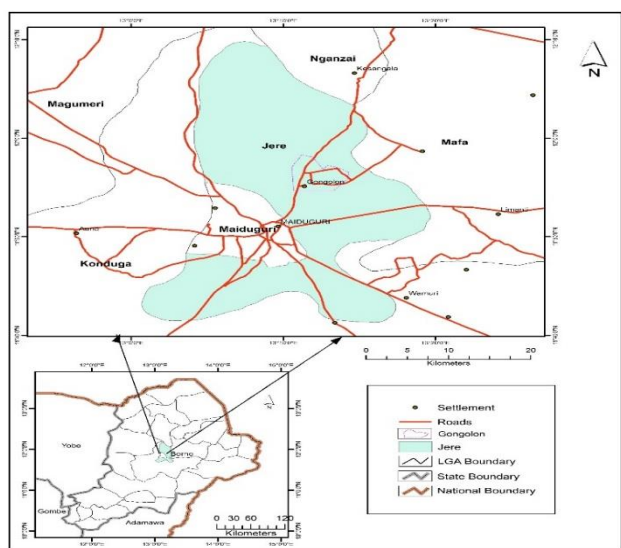
40 is a medium-duration variety recommended for most environments. FARO 40, Narica 1 and Marica 2 are composite developed in Nigeria and are resistant to lodging and diseases. Heavy metals pollution in agricultural soils are harmful to plants, animal and human has becoming a serious concern all over the world [2]. Heavy metal contamination is harmful to plants, animals and human. Heavy metal accumulation is a principal factor in soil quality degradation and reduction of the capacity of the soil to grow healthy plants [3]. Soils may become contaminated from the accumulation of heavy metals through application of fertilizer, animal manures, bio-solids (sewage sludge), compost and pesticides [4]. Heavy metals exist in various forms in the soil but the forms that are available to plants are of greatest importance and include the exchangeable, oxides and hydroxides, carbonate and organic matter bonded metals [5]. The presence of heavy metals pollutants in the soil is of great concern because their absorption by rice plants could put human and animal consumers of these plants or crops at great risk. In addition, it has adverse effects on microbial activities, soil porosity, cation exchange capacity (CEC), mineral composition, seed germination etc. [6]. Agricultural soils within big cities are generally exhibiting high levels of pollution due to the complex mixture of pollutants which might be heavy metals, when compared to agricultural soil within rural areas [7]. One of the importance of wastewater and agrochemical in soil is a rise of yield due to nutrients supplied with wastewater as well as soil texture improved by organic matters in wastewater [7], but there have been growing concerned about the use of wastewater and agrochemicals for agricultural production around the world [7]. Also, study all over the world have demonstrated that agricultural soils have become a particularly good tools for diagnosis of pollutants that influence on human health [7]. These concerned is due to the adverse effect on soil due to accumulation of heavy metals by plants that are harmful and toxic to human and animals due to anthropogenic activities especially wastewater [8]. Literature have shown that heavy metals are the leading causes of a several health problems in humans which includes disorders central nervous, prostate cancer, bone marrow hyperplasia, kidney and liver problems and anemia and many other diseases, the literature also demonstrated that heavy metals can results to risk in human through ingestion, dermal and inhaled from soil contact [7,9] Zabarmari and Bulamari are primarily agricultural locations with intense usage of agrochemical and wastewater for cultivation of vegetables and cereals including rice. Agricultural activities have impacted negatively on the soil because bioaccumulation and bio-concentration of the heavy metals in the soil can reach toxic levels even at low exposure. Wastewater from River Ngada is often used for the irrigation of agricultural soil within the Zabarmari and Bulamari agricultural areas to enhance rice productions. The river receives copious

amounts of wastewater from residential houses and abattoirs sited along its course, wastewater from industries, solid waste and other waste within the Maiduguri metropolis are discharged directly into the river. Literature within the study area have demonstrated that urban waste management and garbage disposal practices in the city are very poor, and these garbage and wastewater from the Municipal contains large amounts of heavy metals which are responsible for the pollution of the river [10]. Study by [10] concluded that the current water quality status of river Ngada posed both environmental and health hazards for agricultural production and further recommended the need for immediate remediation programme to ameliorate the poor water status of this portion of the river that is used for the irrigation of agricultural soil. A research conducted in the study areas by [11] revealed higher concentration of heavy metal in all the soil samples, their concentrations were much more than the WHO, 2010 limit. Their findings further revealed that the used of sewage waste from residential areas and wastewater for agricultural cultivation within the study areas are the main culprit for the high levels of heavy metals detected. All over the world including Africa, several studies have been carry out on soil vegetable metal concentrations, potential ecological risk, cancer and non-cancer risk assessment by [7, 12, 13, 14, 15, 16, 17, 18, 19]. Few studies have also been carried out within the study areas on the levels of heavy metals in soil and vegetables [11]. Also, the have been growing concern about the increase cases of kidney diseases and cancer related illness in the study area, and some studies are ongoing in other food products. However, information and study about the risk associated with serious effect of heavy metals contamination in relation to children and adult in soil and rice samples are lacking in the study areas. Due to the urgent needs and demand for food production in the study areas in other to meet the ever increasing population within the metropolis as result of push factors by insurgency, and the urgent need to find the root course of kidney and cancer related illness within the State. This study is aim at: (i) determine the concentrations of heavy metals in the soil and varieties of rice samples (ii) evaluate the heavy metal pollution using potential ecological risk, adverse effect index, Geo-accumulation load index, contamination factor and pollution load index (iii) assessed human health risk assessment of heavy metals (non-carcinogenic and carcinogenic health risk).

2. Materials and Methods

The study area is Zabarmari and Bulamari agricultural locations in Jere Local Government Area, Borno State, North Eastern Nigeria Map 1. The study areas lies within the latitudes 11o40'N and 12o05'N and longitudes 13o50'E and 12o20'E. According to method adopted by [20]. Soil samples were collected from the Zabarmari and Bulamari agricultural locations and are done at three different

depths (0-5 cm, 5-10 cm and 10-15 cm), by using spiral auger of 2.5 cm diameter. Each of the soil samples from different depth were pulled together to form a representation of each depth. The soil samples were placed in a clean plastic bags and transported to the Department of Pure and Applied Chemistry Laboratory, University of Maiduguri. Samples were collected for a period of four months. Rice samples were collected in accordance with the method as adopted by [20]. The developed varieties of rice in Nigeria which include Narica 1, Marica 2, De-gold and Faro 44 were collected from each of Zabarmari and Bulamari in Jere Local Government Area, Borno State, North Eastern Nigeria. The different varieties of rice samples collected were transported to the laboratory and stored at 25oC.



Map 1: Map of Maiduguri Showing the Study Area

2.1 Preparation of Soil Samples

The soil samples were air dried under laboratory condition. The dried soil was then grounded to fine particles using a plastic mortar and pestle. It was sieved using a 2 mm mesh sieve and stored, ready for digestion. This procedure was repeated for all the soil samples.

2.2 Preparation of Rice Samples

The rice sample were threshed, and the husk were manually removed with hand and dried under laboratory condition and ground with plastic mortar and pestle, and sieved with a 2 mm mesh, and stored, ready for digestion. This procedure was repeated for all the varieties of rice samples.

2.3 Digestion of Soil and Rice Samples for Heavy Metals Determination

Two grammes each of the soil samples were weighed into acid washed glass beaker. The samples were digested by the addition of 20cm³ of aqua regia (mixture of HCl and HNO₃, ratio 3:1) and 10cm³ of 30% H₂O₂. The H₂O₂ were added in small portions to avoid any possible overflow leading to loss of material from the beaker. The beakers were covered with watch glass and heated over a

hot plate at 90oC for two hours. The beaker wall and watch glass were washed with distilled water and the samples were filtered out to separate the insoluble solid from the supernatant liquid. The volumes were adjusted to 100cm³ with distilled water. This procedure was repeated for all the soil and varieties of rice samples collected.

2.4 Elemental Analysis of Samples

Analysis for the determination of Hg, As, Pb, Cd, Ni and Cr were carried out directly on each final solution using Perkin Elmer analyst 300 atomic absorption spectroscopy (AAS).

2.5 Statistical Analysis

Data collected were subjected to one way analysis of variance (ANOVA) and probabilities less than 0.05 were considered significant.

2.6 Quality Control and Quality Assurance

The quality assurance and quality control were performed to confirm the accuracy of the methods used for analysis using spike recovery method. The spike recovery was done by adding a known amount of analyte concentration and analyzing it again [21]. Recovery were ranged between 90.91% to 96.87%. Black was analyzed after the analysis of 7 samples of the soil and rice is digested. The LOD in mg/kg for Hg, As, Pb, Cd, Ni and Cr were 0.0003, 0.001, 0.004, 0.0003, 0.004 and 0.002 respectively, while LOQ in mg/kg for Hg, As, Pb, Cd, Ni and Cr were 0.001, 0.004, 0.01, 0.001, 0.01 and 0.01.

2.7 Evaluation of Heavy Metals Contamination in Soil

2.7.1 Potential Ecological Risk

Potential ecological risk is used to assess heavy metals toxicity and it is used in the present study to estimate soil heavy metals levels. Equation i to iii was used to calculate the Potential ecological risk.

$$C_f^i = C_s^i / C_n^i \quad \text{Eq. 1}$$

$$E_r^i = T_r^i \times C_f^i \quad \text{Eq. 2}$$

$$RI = \sum_{r=1}^n E_r^i \quad \text{Eq. 3}$$

C_fⁱ is the contamination coefficient, C_sⁱ represents metal content in soil, and C_nⁱ is the regional background value for heavy metals (As = 7.7, Cd = 0.119, Cr = 60.8, Ni = 24.7, Pb = 23.7 and Hg =0.77). Where RI represent the sum of all risk factors for heavy metals in the soil, E_rⁱ is the ecological risk of individual metals, T_rⁱ is toxic response factor: Hg = 40, As = 10, Pb = 5, Ni = 5, Cd = 30 and Cr = 2 [22]. The E_rⁱ and RI classifications are presented in Table 3.

Table 1: Ecological risk of individual metal and potential ecological risk grades [22]

E_r^i value	Grades of ecological risk of individual metals	RI value	Grades of potential ecological risk of the environment
$E_r^i < 40$	Low risk	$RI < 150$	Low risk
$40 \leq E_r^i < 80$	Moderate risk	$150 \leq RI < 300$	Moderate risk
$80 \leq E_r^i < 160$	Considerable risk	$300 \leq RI < 600$	Considerable risk
$160 \leq E_r^i < 320$	High risk	$RI \geq 600$	Very high risk
$E_r^i \geq 320$	Very high risk		

2.7.2 Adverse Effect Index

The extents of the adverse effects (AEI) of the study metals on the benthic biota were assessed by comparing total concentrations of individual heavy metals to their threshold effect levels [23, 24] as follows:

$$AEI = \frac{TEL}{[Mi]} \quad \text{Eq. 4}$$

[Mi] = concentration of the heavy metal
 TEL = Threshold Effect Level of the metal.
 TEL values =: As = 7.2, Cd = 0.68, Cr = 52.8, Hg = 0.174, Pb = 30.2 and Ni = 25.7 mg/kg respectively [25].
 If AEI is less than 1 = concentration of a metal is not high enough to cause adverse effects to the benthic organisms. If AEI value greater than 1 = suggests that the metal could cause adverse biological effects.

2.7.3 Geo-accumulation Load Index (I-geo)

Geo-accumulation index (I-geo) by [26] was used to evaluate the magnitude of contaminants in the soil profile and intensity of heavy metal pollution in the soil profile at the different depths, equation:

$$I_{geo} = \log_2 (C_n / 1.5B_n) \quad \text{Eq. 5}$$

Where, C_n is the concentration of element 'n', B_n is the geo-accumulation background value and 1.5 is the background matrix correction factor due to lithogenic effects. The background values used in the present study were in mg/kg: 0.77 for Hg, 7.7 for As, 20 for Pb, 7.5 for Cd, 68 for Ni and 90 for Cr. The geo-accumulation index (I-geo) scale consists of the following grades:

2.7.4 Contamination Factor

The contamination factor was used to determine the contamination status of the soil and is calculated according to:

$$CF = C_{metal} / C_{background} \quad \text{Eq. 6}$$

CF is contamination factor
 C_{metals} is concentration of heavy metals in soil

C background is the background values of the metal heavy metals. The contamination factor are classified into four groups: $CF < 1$ refers to the low contamination factor; $1 \leq CF < 3$ refers to the moderate contamination factor; $3 \leq CF < 6$ refers to considerable contamination factors; $CF \geq 6$ refers to the very high contamination factor [22]. Pollution load index of soil was developed by [27], and it is calculated by obtaining the n-root from the n-CFs that was obtained for all the metals as follows:

$$PLI = \sqrt[n]{(CF_{Hg} \times CF_{As} \times CF_{Pb} \times CF_{Cd} \times CF_{Ni} \times CF_{Cr})} \quad \text{Eq. 7}$$

Table 2: Geochemical Index (I-geo) in Relation to Pollution Intensity

I _{geo}	Risk category
$I_{geo} \leq 0$	Practically unpolluted
$0 \leq I_{geo} \leq 1$	Unpolluted to moderately polluted
$1 \leq I_{geo} \leq 2$	Moderately polluted
$2 \leq I_{geo} \leq 3$	Moderately to strongly polluted
$3 \leq I_{geo} \leq 4$	Strongly polluted
$4 \leq I_{geo} \leq 5$	Strongly to extremely polluted

The PLI represents the number of times by which the metal content in the soil exceeds the average natural background concentration and it further gives a summative indication of the overall level of heavy metal toxicity in a sample. If the PLI value is > 1 the environment is polluted, If PLI is < 1 its indicates no pollution, if PLI = 1, its indicate heavy metal loads close to the background level [27].

2.7.5 Human Health Risk Assessment of Heavy Metals in Soil

The health risk assessment is centered on the exposure factors and guidelines handbook [28] as adopted by [29]. The study heavy metals were identified as potential contaminants regarding human health. Based on the daily activities of the farmers, they might be exposed to soil heavy metals through soil ingestion, dermal and inhalation contact. Average daily dose values (ADD) of

contaminants were calculated using the equation below in different exposure pathways as adopted by [30] and the values of the parameters are also highlighted below.

$$ADD_{ing} = \frac{C \times IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad \text{Eq. 8}$$

$$ADD_{inh} = \frac{C \times InhR \times EF \times ED}{PEF \times BW \times AT} \quad \text{Eq. 9}$$

$$ADD_{dermal} = \frac{C \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad \text{Eq. 10}$$

2.7.6 Non-carcinogenic Risk Assessment

Non-carcinogenic risk assessment was evaluated by using hazard quotient (HQ) and hazard index (HI) [34] as adopted by [29]. According to [32], hazard quotients represent a ratio of the exposure dose for each heavy metal divided by an oral chronic reference dose (RfD). If $HQ < 1$, no adverse effects occur; $HQ > 1$, signifies adverse effects [31].

$$HQ = \frac{ADD}{RfD} \quad \text{Eq. 11}$$

In order to evaluate the overall adverse effects of non-carcinogenic risk, hazard index approach was used [32]. The HI is the sum of HQ through the exposure pathways for heavy metals. If $HI < 1$ it denotes non-carcinogenic effects, whereas if $HI > 1$ it signifies adverse effects.

$$HI = \sum HQ_i \quad \text{Eq. 12}$$

2.7.7 Carcinogenic Risk Assessment

carcinogenic risk assessment is the possibility of an individual to develop cancer related illness during the lifetime exposure to the carcinogenic threats [29]. According to [32] and as adopted by [29], the total cancer risk is arrived at by multiplication of cancer slope factor (SF) by ADD of contaminant exposed over a lifetime risk of an individual developing cancer related illness.

$$\text{Risk} = ADD \times SF \quad \text{Eq. 13}$$

2.7.8 Human Health Risk Assessment of Heavy Metals in Rice

The hazard quotient (HQ) and hazard index (HI) of heavy metals were used to estimate the non-carcinogenic risk of consumption of rice by the population [39]

$$EDI = \frac{C \times IR \times ED \times EF}{BW \times AT} \quad \text{Eq. 14}$$

According to [39], hazard quotients represent a ratio of the exposure dose for each heavy metal divided by an oral chronic reference dose (RfD). If $HQ < 1$, no adverse effects occur; $HQ > 1$, signifies adverse effects [31].

$$HQ = \frac{EDI}{RfD} \quad \text{Eq. 15}$$

The oral reference doses (RfD) used for each of the metals in mg/kg/day are $Hg = 1.0 \times 10^{-4}$, $As = 3.0 \times 10^{-4}$, $Pb = 4.0 \times 10^{-3}$, $Cd = 1.0 \times 10^{-3}$, $Ni = 2.0 \times 10^{-2}$ and $Cr = 1.5$ [39]. In order to evaluate the overall adverse effects of non-carcinogenic risk, hazard index approach was used [32]. The HI is the sum of HQ through the three exposure pathways for heavy metals. If $HI < 1$ non-carcinogenic effects is unlikely to occur, whereas if $HI > 1$ it signifies adverse non-carcinogenic effects are likely to occur [39].

$$HI = HQ_1 + HQ_2 + HQ_3 + \dots + HQ_n \quad \text{Eq. 16}$$

3. Results and Discussion

3.1 Concentration of Heavy Metals in Agricultural Soil

3.1.1 Mercury (Hg)

The Concentrations of Hg in all the soil samples from different depth within the two sampling locations is as presented in Table 6 and 7. The highest Hg level was detected at the point S1 agricultural location with values ranging from 0.76 ± 0.01 to 2.12 ± 0.03 mg/kg with an average value of 1.37 ± 0.02 mg/kg, while the point S2 location recorded the least values ranging from 0.12 ± 0.03 to 0.41 ± 0.02 mg/kg with an average value of 0.22 ± 0.02 mg/kg. Comparing with the present finding, [12] reported lower concentration of Hg in different mine soil with values ranging from 0.06 to 0.13 mg/kg with an average of 0.09 mg/kg. Similar study was also conducted by [40] in soils samples from Korle Lagoon area in Accra, Ghana, and their finding also revealed lower level of Hg with values ranging from 0.03 to 0.67 mg/kg. The concentrations of Hg decrease with increased in depth and was below the [41] limit of 2.00 mg/kg, with exception of 0-5 cm depth which was higher than the said limit. 3.1.2 Arsenic (As)

The mean concentration of As in the soil samples from the two agricultural locations are as presented in Table 6 and 7, with values ranging from 2.44 ± 0.01 to 7.21 ± 0.07 mg/kg with an average value of 4.96 ± 0.04 mg/kg from point S1 Location, while point S2 Locations recorded 1.68 ± 0.02 to 5.21 ± 0.11 mg/kg with an average of 3.11 ± 0.06 mg/kg. The presence of As in the soil at the various depth could be attributed to the occurrence in the wastewater samples used for the irrigation of the farm land as reported by [11]. Similar study were reported by [40] with values ranging from 0.04 to 3.67 mg/kg in soils samples from Korle Lagoon area in Accra, Ghana; [2], with values ranging from 0.99 to 9.01 mg/kg in soil samples from Tarutia, Tangail Sadar Upazila of Tangail

Table 3: Parameters Values for Human Health Risk Assessment of Heavy Metals in Soil Samples

Parameters	Highlight of Parameters	Children Values	Adult Values
C	Concentrations	Present Study	Present Study
IngR	Ingestion Rate	200 mg/day	100 mg/day
EF	Exposure frequency	350 days/year	350days/year
ED	Exposure duration	6 years	24 years
BW	Body weight	15 kg	56.8 kg
AT	Average time	365 x ED	365 x ED
SA	Skin surface area exposed to soil contact	1600 cm ²	4350 cm ²
AF	Soil to Skin adherence factor	0.2 mg/cm/day	0.7 mg/cm/day
ABS	Absorption factor	0.001	0.001
InhR	Inhalation rate	7.63 m ³ /day	12.8 m ³ /day
PEF	Particle emission factor	1.36x10 ⁹ m ³ /kg	1.36 x 10 ⁹ m ³ /kg

Parameters and values used for this study are references as follows: IngR = [31], EF = [29], ED = [31], BW = [29], AT = [32], SA = [29], AF = [33], ABS = [29], InhR = [29], PEF = [31].

Table 4: Oral Reference Dose and Cancer Slope Factor Values for Heavy Metals

Metals	References doses (mg/kg/day)			Slope factors (mg/kg/day)		
	Ingestion	Inhalation	Dermal	Ingestion	Inhalation	Dermal
Hg	3.00E-04	3.00E-04	3.00E-04			
As	3.00E-04	1.50E-05	9.00E-04	1.50	15.1	3.66
Pb	3.50E-05	3.52E-03	5.20E-04	8.50E-03		
Cd	1.00E-03	1.50E-05	1.00E-05		6.3	
Ni	2.00E-02	9.00E-05	9.00E-05	0.84	0.84	
Cr	3.00E-03	2.86E-05	6.00E-05		42.0	

Sources: [35, 36, 37, 38] as adopted by [13].

Table 5: Parameters Values for Human Health Risk Assessment of Heavy Metals [39]

Parameters	Highlight of Parameters	Values
EDI	Estimated daily intake	To be calculated
C	Concentration	Present study
IR	Ingestion rate	0.063
ED	Exposure duration	70 years
EF	Exposure frequency ³	365 days/year
BW	Average body weight	70kg
AT	Average time	365 day/year x ED

District, Bangladesh; [12] in Johannesburg, Gauteng Province, South Africa with values ranging from 65.17 to 115.19 mg/kg with an average of 79.40 mg/kg; [30], in soil samples from Hunan Province, China with average value of 84.27 mg/kg [42], with values ranging from 3.33 to 28.04 mg/kg in Mongalia. The above findings were higher than the that of the presence study, with exception of that of [40]. The concentration of As at point S1 and S2 were below the WHO/FAO (2001) permissible limit

of 20.00 mg/kg as cited by [40].

3.1.2 Arsenic (As)

The mean concentration of As in the soil samples from the two agricultural locations are as presented in Table 6 and 7, with values ranging from 2.44±0.01 to 7.21±0.07 mg/kg with an average value of 4.96±0.04 mg/kg from point S1 Location, while point S2 Locations recorded 1.68±0.02 to 5.21±0.11 mg/kg with an average of

3.11±0.06 mg/kg. The presence of As in the soil at the various depth could be attributed to the occurrence in the wastewater samples used for the irrigation of the farm

land as reported by [11]. Similar study were reported by [40] with values ranging from 0.04 to 3.67 mg/kg in soils samples from Korle Lagoon area in Accra, Ghana; [2],

Table 6: Concentrations of Heavy Metals in Soil Samples from Different Depth of Point S₁ Agricultural Location

Depth	Concentrations (mg/kg)					
	Hg	As	Pb	Cd	Ni	Cr
0-5cm	2.14 ^a ±0.03	7.21 ^a ±0.07	6.21 ^a ±0.09	3.21 ^a ±0.02	4.54 ^a ±0.10	9.32 ^a ±0.21
5-10cm	1.21 ^b ±0.02	5.24 ^b ±0.03	3.21 ^b ±0.05	2.14 ^b ±0.01	2.87 ^b ±0.05	5.44 ^b ±0.10
10-15cm	0.76 ^c ±0.01	2.44 ^c ±0.01	1.87 ^c ±0.03	1.01 ^c ±0.01	1.66 ^c ±0.02	1.64 ^c ±0.04
Average	1.37±0.02	4.96±0.04	3.76±0.06	2.12±0.01	3.02±0.06	5.47±0.12

Within Columns Mean with different letters are statistically different, P< 0.0

S₁ = Zabarmari Agricultural Location

Table 7: Concentrations of Heavy Metals in Soil Samples from Different Depth of Point S₂ Agricultural Location

Depth	Concentrations (mg/kg)					
	Hg	As	Pb	Cd	Ni	Cr
0-5cm	0.41a±0.02	5.21a±0.11	4.24a±0.21	2.31a±0.06	3.21a±0.14	7.21a±0.22
5-10cm	0.14b±0.01	2.45b±0.06	1.86b±0.14	1.44b±0.02	1.24b±0.07	3.66b±0.15
10-15cm	0.12c±0.03	1.68c±0.02	1.23c±0.05	1.04c±0.01	1.03c±0.04	1.76c±0.02
Average	0.22±0.02	3.11±0.06	2.44±0.13	1.60±0.03	1.83±0.08	4.21±0.13

Within Columns Mean with different letters are statistically different, P< 0.05

S₂ = Bulamari Agricultural Location

with values ranging from 0.99 to 9.01 mg/kg in soil samples from Tarutia, Tangail Sadar Upazila of Tangail District, Bangladesh; [12] in Johannesburg, Gauteng Province, South Africa with values ranging from 65.17 to 115.19 mg/kg with an average of 79.40 mg/kg; [30], in soil samples from Hunan Province, China with average value of 84.27 mg/kg [42], with values ranging from 3.33 to 28.04 mg/kg in Mongalia. The above findings were higher than the that of the presence study, with exception of that of [40]. The concentration of As at point S1 and S2 were below the WHO/FAO (2001) permissible limit of 20.00 mg/kg as cited by [40].

3.1.3 Lead (Pb)

The concentrations of (Pb) in soil samples ranged from 1.87±0.03 to 6.21±0.02 mg/kg with an average value of 3.76±0.06 mg/kg point S1 agricultural location, point S2 location ranged from 1.23±0.05 to 4.24±0.21 mg/kg with an average value of 2.44±0.13 mg/kg Table 6 and 7. Point S1 which received much more pollution load recorded the highest Pb concentrations as compared to point S2. The concentration of Pb recorded in this study were lower than the ranged of 20.90 to 43.11 mg/kg as reported by

[42] in soil samples from Mongolia; [7], with values ranging from 5.04 to 239.04 mg/kg in soil samples from Ijebu-Ode, Nigeria; [8], in soil samples from Ashaka, Nigeria with values ranging from 6.10 to 37.20 mg/kg; [43] with values ranging from 14.65 to 47.04 mg/kg in Itakpe and Agbaji, Nigeria, and 784.05 mg/kg as reported by [30], in soil samples from Hunan Province, China; [44] also recorded 23.30 mg/kg of Pb in soil from central Gansu Province of China. [45] in their study recorded value for Pb between 1.5 and 888 mg/kg in soils of Ontario. [46] also recorded Pb levels at 21.3 mg/kg of Pb in soil. [2] recorded 2.83 mg/kg to 81.43 mg/kg Pb in agricultural soil Tarutia, Tangail Sadar Upazila of Tangail District, Bangladesh. The recorded concentration of Pb in the two agricultural locations were lower than the [41] permissible limit of 50.00 mg/kg as cited by [40].

3.1.4 Cadmium (Cd)

The mean concentration of Cd at point S1 agricultural location 1.01±0.01 to 3.21±0.02 mg/kg with an averaged of 2.12±0.01 mg/kg, while point S2 agricultural location ranged from 1.04±0.01 to 2.31±0.06 mg/kg with an average of 1.60±0.03 mg/kg. Results of Cd from the

presence study is in line with the finding of [12] who reported an average value of 0.05 mg/kg mg/kg in soil samples from Witwatersrand Gold Mining Basin, South Africa. The concentration of Pb obtained at S1 and S2 was within the [41] permissible limit of 3.0 mg/kg as cited by [40].

3.1.5 Nickel (Ni)

The concentrations of nickel recorded in the soil sample from point S1 ranged from 1.66±0.02 to 4.54±0.10 mg/kg with an average value of 3.02±0.06 mg/kg, while point S2 ranged from 1.03±0.04 to 3.21±0.14 mg/kg with an average value of 1.83±0.08 mg/kg. However, the results of the present study is lower than values reported by [47] in soil samples from China; [2], also reported values of Ni ranging from 8.75 to 87.72 mg/kg in soil from Tarutia, Tangail Sadar Upazila of Tangail District, Bangladesh. The concentration of Ni recorded at the various sampling points were much more below the [41] permissible limit of 50 mg/kg as cited by [40].

3.1.6 Chromium (Cr)

The concentration of chromium Cr ranged from 1.64±0.04 to 9.32±0.21 mg/kg at point S1 with average value of 5.47±0.12 mg/kg, while that of point S2 ranged from 1.76±0.02 to 7.21±0.22 mg/kg with an average value of 4.21±0.13 mg/kg. Results of the presence study were relatively lower than values from other studies as highlighted by [44] recorded 40.10mg/kg Cr in the agricultural soil in Gansu Province of China. [48] reported average Cr concentration in soil samples at DEPZA with value of 2753.20 mg/kg. Also, the level of Cr which ranged from 5.00 to 1,500.00 mg/kg was detected in Canadian soils by [49]. [45] recorded 14.30 mg/ kg Cr in soils samples from Ontario. [2] recorded 13.22mg/kg and 13.26 mg/kg Cr in agricultural soil Tarutia, Tangail Sadar Upazila of Tangail District, Bangladesh.

3.2 Concentration of Heavy Metals in Varieties of Rice

The mean concentrations of the studied heavy metals were determined in all the varieties of rice samples collected from the two agricultural location (Table 8 and 9). The highest concentration of Hg was detected at point S1 agricultural location with values ranging from 0.87±0.01 to 1.23±0.02 mg/kg, while point S2 showed the least concentration ranged of 0.06±0.01 to 0.27±0.02mg/kg. Narica variety was able to present the highest accumulation value of Hg (0.27±0.02 to 1.23±0.02 mg/kg), while De-gold variety shows the least ranges (0.08±0.01 to 0.87 mg/kg) for both locations. The results of Hg in the presence study was however lower than the 0.014 mg/kg, 0.006 mg/k, 0.005 mg/kg, 0.002 mg/kg and 0.0094 mg/kg as detected in rice samples by

[50] Yangtze River Delta, China; [51] in China; [52] in industrial zone in Jiangsu, China and [53] in Zhejiang, China; [54] in Ugbawka fields, Enugu, Nigeria and [55] in Monrovia respectively. The concentrations of Hg in all the varieties of rice were relatively higher than the maximum limit of 0.05mg/kg as reported by [1]. Although the level of Hg in the different varieties of rice studied is low. However, Hg in elemental form and its methylmercury are known to be toxic to the central and peripheral nervous systems even at low concentrations. Also, inhalation of mercury vapour at lower concentration can lead to fatal harmful effects on the central nervous, digestive and immune systems, lungs and kidneys [56].

3.2.1 Arsenic (As)

The values of As in the four varieties of rice from the two agricultural locations ranged from 1.32±0.02 to 4.65±0.03 mg/kg. Significant variation was observed between the level of As in all the varieties of rice samples. The values of As detected in all the rice samples were higher than the [1] permissible limit of 0.01 mg/kg. This result was lower with the values observed in Turkey (0.98 mg/kg) by [57]; Zhejiang, China (0.08 mg/kg) by [52].

3.2.2 Lead (Pb)

The mean concentration of Pb in the varieties of rice from the two agricultural locations ranged between 1.06 to 3.24 mg/kg. Similar levels with that of the presence study were reported by [58] and [59] with their mean levels of 3.99 mg/kg and 3.99 mg/kg respectively. The present level of Pb were also relatively lower than those detected in rice samples by [52], [60]; [53]; [61] with their reported values of 0.005 to 0.220 mg/kg, 0.001 to 1.00 mg/kg, 0.60 mg/kg and 0.097 mg/kg respectively. [62] reported lead adverse effect on nervous system, Hematopoietic System, Renal system, Cardiovascular system and reproductive system. The mean values recorded in all the varieties of rice samples collected were markedly above the [1] acceptable limit of 0.43 mg/kg.

3.2.3 Cadmium (Cd)

The concentration of Cd in the two agricultural locations were found to range from 0.065±0.02 to 1.54±0.01mg/kg Table 8 and 9, with Narica 1 variety of rice showing the highest mean concentration Table 8. [52] reported level of 0.037 mg/kg in rice from Zhejiang, China. Study carried out in rice samples from Iran showed a mean level of 0.062 mg/kg [63]; 0.1 to 0.2 mg/kg by [60] in East Coast of India. In Enugu, 0.45 mg/kg Cd was detected in rice [53]; 1.32 mg/kg was detected in rice grain in Iran by [64]. [65] reported that cadmium causes acute intoxication, Kidney and liver damage, Carcinogenity

Within Columns Mean with different letters are statistically different, P< 0.05

S1 = Zabarmari Agricultural Location

Table 8: Concentrations of Heavy Metals in Rice Samples from Point S₁ Agricultural Location

Samples	Concentrations (mg/kg)					
	Hg	As	Pb	Cd	Ni	Cr
Narica 1	1.23 ^a ±0.02	4.65 ^a ±0.03	3.24 ^a ±0.01	1.54 ^a ±0.01	1.88 ^a ±0.01	3.65 ^a ±0.02
Marica 2	1.07 ^b ±0.01	3.24 ^b ±0.04	2.75 ^b ±0.02	0.87 ^b ±0.02	0.55 ^b ±0.01	1.68 ^b ±0.01
De-gold	0.87 ^c ±0.01	2.04 ^c ±0.01	1.22 ^c ±0.01	0.76 ^c ±0.01	1.54 ^c ±0.02	1.36 ^c ±0.02
Faro 44	1.12 ^d ±0.02	2.98 ^d ±0.02	2.77 ^d ±0.05	0.65 ^d ±0.02	0.94 ^d ±0.01	0.76 ^d ±0.01

Within Columns Mean with different letters are statistically different, P < 0.05

S1 = Zabarmari Agricultural Location

Table 9: Concentrations of Heavy Metals in Rice Samples from Point S₂ Agricultural Location

Samples	Concentrations (mg/kg)					
	Hg	As	Pb	Cd	Ni	Cr
Narica 1	0.27 ^a ±0.02	1.87 ^a ±0.02	2.14 ^a ±0.01	1.24 ^a ±0.02	0.98 ^a ±0.01	3.21 ^a ±0.02
Marica 2	0.11 ^b ±0.01	1.57 ^b ±0.01	1.06 ^b ±0.01	1.07 ^b ±0.01	0.56 ^b ±0.01	2.13 ^b ±0.02
De-gold	0.08 ^c ±0.01	1.32 ^c ±0.02	2.21 ^c ±0.02	0.96 ^c ±0.01	0.82 ^c ±0.02	1.42 ^c ±0.01
Faro 44	0.06 ^d ±0.01	1.66 ^d ±0.01	1.78 ^d ±0.02	0.88 ^d ±0.01	0.64 ^d ±0.01	0.59 ^d ±0.01

Within Columns Mean with different letters are statistically different, P < 0.05

S₂ = Bulamari Agricultural Location

vascular and immune system even at low concentration. However, the mean concentration of Cd in all the varieties of rice samples were higher than the maximum allowable standard permissible limit of 0.02 mg/kg as reported by [1].

3.2.4 Nickel (Ni)

The concentration of nickel in the four varieties of rice from the two-sampling location also ranged from 0.55±0.01 to 1.88±0.01 mg/kg with Narica 1 and Marica 2 varieties showing the highest concentration. The concentration of Ni fell in line with the findings recorded by [53] with a value of 0.60 mg/kg. The concentration of Ni in the rice samples studied exceeded the maximum standard limit of 0.1 mg/kg as describe by [1]. Study carried out by [66], revealed nickel-induced genotoxicity, carcinogenicity, immunotoxicity and toxicity in various metabolically active tissues.

3.2.5 Chromium (Cr)

Chromium concentration from the two agricultural locations were lower than 0.02±0.004 to 0.33±0.049 mg/kg reported by [67]; but higher than values of 37.33 to 111.95 mg/kg reported in vegetables by [58] Table 8 and 9. Also, the values detected in the present study had

similarity with previous study on rice with values ranging from 0.3 to 0.7 mg/kg by [60] in East Coast of India.

However, high level of Cr was observed in rice by [53] in Ugbawka fields, Enugu, Nigeria with a value of 14.17 mg/kg. The level of Cr in all the rice samples were relatively higher than the maximum permissible limit of 0.2 mg/kg as prescribed by [1]. Generally, the concentrations of all the studied metals in the soil samples were significantly higher at a depth of 0-5 cm, while the lowest concentration were observed at a depth of 10-15 cm. Narica 1 and Marica 2 varieties of rice were observed to be higher in term of metal concentrations when compared to other varieties. The high concentrations of all the heavy metals in the soil samples when compared to the rice samples might be because soil act as an important sink and first point of contact with pollutants including heavy metals. The present findings is similar to study conducted by [68, 69, 70, 71, 72, 73, 74] in varieties food for heavy metals analysis. The results of the present study showed a significant increased in concentrations of all the heavy metals when compared to the FAO/WHO standard limits. This is an indication that the wastewater and agrochemicals used for food production has an adverse effect on the population that depend on this rice for consumption.

3.3 Potential Ecological Risk Index of Heavy Metals

The results from potential ecological risk factor (E_{ir}) and risk index (RI) for point S_1 and S_2 are as presented in Table 10. The average values of (E_{ir}) from point S_1 for Hg, As, Pb, Cd, Ni and Cr are 71.17, 6.45, 0.79, 534.45, 0.61 and 0.18 respectively, with an average RI of 613.65. Also, the E_{ir} and risk index (RI) for point S_2 for Hg, As, Pb, Cd, Ni and Cr are 11.60, 4.04, 0.52, 402.52, 0.37 and 0.14 respectively with an average RI of 419.19. Ecological risk of any metal is classified as low risk, if the risk factor (E_{ir}) <40 . The E_{ir} of some of the studied heavy metals (As, Pb, Ni and Cr) for point S_1 and point S_2 (Hg, As, Pb, Ni and Cr) were relatively much less than 40, which indicates low risk. The ecological risk of metal is classified as moderate risk if $40 \leq E_{ir} <80$, considerable risk if $80 \leq E_{ir} <160$, high risk if $160 \leq E_{ir} <320$ and very high risk (dangerous) if $E_{ir} \geq 320$ (Hakanson, 1980). The average E_{ir} of Hg was 71.17 for point S_1 , which is greater than 40 and less than 80, indicating a moderate potential ecological risk. The average E_{ir} for Cd at point S_1 and S_2 ranged from 402.52 to 584.45, these values were greater than 320 ($E_{ir} \geq 320$), indicating that the study areas are extremely high potential ecological risk and dangerous with respect to Cd. [2], also reported E_{ir} value of 889.18 Cd, which is greater than and equal to 320, indicating very high potential ecological risk and dangerous. [22, 75, 76] classifies $RI <150$ to mean low potential ecological risk; $150 \leq RI <300$, meaning moderate ecological risk potential; $300 < RI <600$, meaning considerable ecological risk, and if $RI > 600$; it means very high ecological risk. The average RI value of Cd at point S_1 is 613.65, indicating very high ecological risk. Point S_2 shows 419.19 Cd and less than $RI \geq 600$, indicating considerable ecological risk.

3.4 Adverse Effect Assessment

The adverse effect index (AEI) of heavy metals in point S_1 agricultural location for Hg, As, Pb, Cd, Ni and Cr are 0.15, 1.77, 10.14, 0.40, 10.03 and 15.86 respectively, while that of point S_2 for Hg, As, Pb, Cd, Ni and Cr are 1.03, 2.87, 15.97, 0.47, 17.90 and 17.25 respectively (Table 11). According to adverse effect assessment, If AEI is less than 1, the concentration of metal is not high enough to cause adverse effects to the benthic organisms.

But If AEI value is greater than 1, it suggests that the metal could cause adverse biological effects to benthic organism. Based on the above assessment, the average values of all the heavy metals in soil samples from both points were higher than 1, with exception of Hg at point S_1 and Cd from both sampling point. The results of this study further reveals that, with the average AEI values of 10.03, 15.86 from point S_1 and 17.90, 17.25 from point S_2 , Ni and Cr are most likely to induce adverse biological effects to benthic organism followed by Pb, As, Hg and Cd. [77] reported AEI values of 1.7 As, 1.4 Cd and 1.3 Cd, which are greater than 1. The study further suggests

that the metal could cause adverse biological effects to benthic organism.

3.5 Geoaccumulation Index (I_{geo}) Values in Soil

The geo-accumulation risk index of soil quality was analyzed using I_{geo} index of classification as proposed by [78]. The I_{geo} index of classification involved seven grade, soil can be classified unpolluted if $I_{geo} \leq 0$; unpolluted to moderately polluted if $0 \leq I_{geo} \leq 1$; moderately polluted if $1 \leq I_{geo} \leq 2$, moderate to strongly polluted if $2 \leq I_{geo} \leq 3$; strongly polluted if $3 \leq I_{geo} \leq 4$; strongly to extremely polluted if $4 \leq I_{geo} \leq 5$ and extremely polluted if $I_{geo} \geq 5$. The average I_{geo} values of heavy metals in soil samples from point S_1 were 0.12 Hg, -1.35 As, -3.16 Pb, -1.13 Cd, -5.19 Ni and -4.95 Cr Table 12. The average I_{geo} values of the studied metals were in the order of $Hg > As > Cd > Pb > Cr > Ni$. Mercury with highest average I_{geo} value of 0.12 was grade as class 2, unpolluted to moderately polluted if $0 \leq I_{geo} \leq 1$ and further indicating the accumulation of Hg in the studied soil. In the case of As, Pb, Cd, Ni and Cr with soil I_{geo} values of -1.35, -3.16, -1.13, -5.19 and -4.95 respectively were classified as class zero ($I_{geo} \leq 0$ (unpolluted)), the results further revealed that the soil samples in relation to As, Pb, Cd, Ni and Cr was not polluted. For point S_2 , the average I_{geo} values of -2.60 Hg, -2.06 As, -3.81 Pb, -2.90 Cd, -5.99 Ni and -5.23 Cr were rank as class zero (that is less than zero $I_{geo} \leq 0$), the results further suggested that the soil samples from point S_2 were not polluted. Similar finding and classification of less than zero $I_{geo} \leq 0$ was detected by [79], in Group B soil samples with I_{geo} values of -0.3 Pb, -0.8 Ni, -0.3 Cd, -1.2 Cr and -0.4 Hg. However, the I_{geo} values for Pb (0.8) for group A and Hg (0.3 to 0.6) group C soil which rank as Class 1 ($0 \leq I_{geo} \leq 1$), indicating unpolluted to moderately polluted contradict that of the present study. Results from the present study showed that all the studied metals in the soil from the two sampling locations are within the background concentrations, with exception of Pb which was moderately polluted. Also, results of I_{geo} further demonstrated that there was minimal contribution of heavy metals from anthropogenic activities in the study locations.

3.6 Contamination Factors (CF) and Pollution Load Index (PLI) in Soil

The values of contamination factor (CF) of the studied metals are as presented in Table 13.

The average contamination factor values of heavy metals in soil samples from point S_1 were 1.78 for Hg, 0.65 As, 0.19 Pb, 0.28 Cd, 0.04 Ni and 0.06 Cr. The average metals CF values were in the order of $Hg > As > Cd > Pb > Cr > Ni$. The contamination factor are classified into four groups: $CF < 1$ refers to the low contamination factor; $1 \leq CF < 3$ refers to the moderate contamination factor; $3 \leq CF < 6$ refers to considerable contamination factors; $CF \geq 6$ refers to the very high contamination factor [22]. Mercury

Table 10: Calculated Ecological Risk Indices of Individual Heavy Metals (E_r^i) and Ecological Risk Indices in Soil Samples

Depth	S_1							S_2						
	E_r^i							E_r^i						
	Hg	As	Pb	Cd	Ni	Cr	RI	Hg	As	Pb	Cd	Ni	Cr	RI
0-5 cm	111.17	9.36	1.31	809.24	0.92	0.31	932.31	21.3	6.77	0.89	582.35	0.65	0.24	612.2
5-10cm	62.86	6.81	0.68	539.5	0.58	0.18	610.6	7.27	3.18	0.39	363.03	0.25	0.12	374.24
10-15cm	39.48	3.17	0.39	254.62	0.34	0.05	298.06	6.23	2.18	0.26	262.18	0.21	0.06	271.13
Average	71.17	6.45	0.79	534.45	0.61	0.18	613.66	11.60	4.04	0.51	402.52	0.37	0.14	419.19

Table 11: Adverse Effect Indices (AEI) of Potentially Harmful Heavy Metals

Depth	S_1						S_2					
	Hg	As	Pb	Cd	Ni	Cr	Hg	As	Pb	Cd	Ni	Cr
0-5 cm	0.08	1.00	4.86	0.21	5.66	5.67	0.42	1.38	7.12	0.29	8.01	7.32
5-10cm	0.14	1.37	9.41	0.32	8.95	9.71	1.24	2.94	16.24	0.47	20.73	14.43
10-15cm	0.23	2.95	16.15	0.67	15.48	32.2	1.45	4.29	24.55	0.65	24.95	30.00
Average	0.15	1.77	10.14	0.40	10.03	15.86	1.04	2.87	15.97	0.47	17.90	17.25

S_1 = Zabarmari Agricultural Location

S_2 = Bulamari Agricultural Location

Table 12: Geoaccumulation Index (Igeo) Values for Heavy Metals in Soil Samples

Depth	S_1						S_2					
	Hg	As	Pb	Cd	Ni	Cr	Hg	As	Pb	Cd	Ni	Cr
0-5 cm	0.89	-0.68	-2.27	-0.69	-4.49	-3.86	-1.49	-1.15	-2.82	-2.28	-4.99	-4.23
5-10cm	0.07	-1.14	-3.22	-0.94	-5.15	-4.63	-3.04	-2.24	-4.01	-2.97	-6.36	-5.20
10-15cm	-0.60	-2.24	-4.00	-1.77	-5.94	-6.36	-3.27	-2.78	-4.61	-3.44	-6.63	-6.26
Average	0.12	-1.35	-3.16	-1.13	-5.19	-4.95	-2.60	-2.06	-3.81	-2.90	-5.99	-5.23

S_1 = Zabarmari Agricultural Location

S_2 = Bulamari Agricultural Location

Table 13: Contamination Factor (CF) and Pollution Load Index (PLI) of Heavy Metals in Soil Samples

Depth	S_1							S_2						
	CF_{Hg}	CF_{As}	CF_{Pb}	CF_{Cd}	CF_{Ni}	CF_{Cr}	PLI	CF_{Hg}	CF_{As}	CF_{Pb}	CF_{Cd}	CF_{Ni}	CF_{Cr}	PLI
0-5 cm	2.78	0.94	0.31	0.43	0.07	0.1	0.37	0.53	0.68	0.21	0.31	0.05	0.08	0.21
5-10cm	1.57	0.68	0.16	0.29	0.04	0.06	0.22	0.18	0.32	0.09	0.19	0.02	0.04	0.10
10-15cm	0.99	0.32	0.09	0.13	0.02	0.02	0.11	0.16	0.22	0.06	0.14	0.02	0.02	0.07
Average	1.78	0.65	0.19	0.28	0.04	0.06	0.23	0.29	0.41	0.12	0.21	0.03	0.05	0.13

S_1 = Zabarmari Agricultural Location

S_2 = Bulamari Agricultural Location

with an average value of 1.78 is classified as group 2 ($1 \leq CF < 3$ which refers to as moderate contamination factor, indicating the contamination of point S_1 soil samples by Hg. In the case of As, Pb, Cd, Ni and Cr, the CF values were less than 1, indicating low contamination. For point S_2 , the average CF values of 0.29 Hg, 0.14 As, 0.12 Pb, 0.21 Cd, 0.03 Ni and 0.05 Cr were rank as group one (1) contaminant (that is less than 1 $CF < 1$), the results

further suggested that the soil samples from point S_2 were not contaminated by the studied heavy metals. Pollution load index of soil was developed by [27], and it is calculated by obtaining the n-root from the n-CFs. $PLI \leq 1$ Unpolluted, $1 \leq PLI \leq 2$ Unpolluted to moderately polluted, $2 \leq PLI \leq 3$ Moderately polluted, $3 \leq PLI \leq 4$ Moderately to highly polluted, $4 \leq PLI \leq 5$ Highly polluted and $PLI > 5$ Very highly polluted [27]. Results

from the present study revealed that the PLI values of As, Pb, Cd, Ni and Cr, fell within the $PLI \leq 1$ category. Indicating no pollution of the studied soil. Hence, the results further give an information that the occurrences of these metals in the earth crust is very minimal and the pollution of the soil by these metals is low.

3.7 Health Risk Assessment of Heavy Metals in Soil

3.7.1 Average Daily Dose

The average daily dose (ADD) values for the present study through the three exposure routes (Ingestion, Inhalation and dermal) for children and adult are as presented in Table 14. The values of ADD ingestion for both agricultural locations for children and adult ranged from $3.77E-07$ to $6.99E-06$, with Cr showing the highest ADDing in children, while Hg showed the least in adult. Also, the ADDinh values for both locations ranged from $7.35E-04$ to $1.63E-02$, with As having the highest ADD, while Hg showed the least. The ADDdermal values for the two agricultural locations ranged from $4.57E-09$ to $2.81E07$, with Cr showing the highest value, and Hg with least value. In comparison of the ADD values for all the studied metals with their individual RfDs via the three routes of exposure showed that the ADD values for both children and adult for ingestion and dermal were lower than their individual RfDs. This finding further demonstrated that, both children and adult population are not under any threat from non-carcinogenic risk as a result of metal contamination. The ADD values via inhalation for both children and adult were higher than the RfDs values for all the studied metals. This call for concerned because both children and adult are under health risk of non-cancer related illness, and the soil ADDinh is the most dominant pathway for the exposure of metals for both children and adult population. Results from the present study further demonstrated that children are more exposed to contamination by heavy metals as compared to adult, such variation might be due to the regular hand-to-mouth habits as observed in children. Similar trend as detected by [13, 43], reported high ADDing and ADDinh in children as compared to adult in soil samples. The present study also demonstrated that in ADDdermal adult showed the highest values of all the studied metals as compared to children. Similar trend was observed in a study conducted by [29], were adult are more exposed to contamination by metals through dermalcontact than children. Coumarin constitutes one of the great classes of natural compounds. In the well-known family of coumarins, dimeric coumarins (bis coumarins) occupy an interesting position. Although some types of these compounds could be extracted from plants [1] and interest in its chemistry because of its fitness as pharmaceutically activities.

3.7.2 Hazard Quotient (HQ) and Hazard Index (HI)

Results of hazard quotient (HQ) and hazard index (HI) are as presented in Table 15. HQ and HI values of less

than 1 means that there is no risk to the population, but if HQ and HI are more than 1, there is case for concern for potential non-cancer adverse effect. Results for children and adult population showed that the calculated values of HQ and HI for all the metals studied were less than 1 (one) for ingestion and dermal pathways. The present study further revealed that there is no non-carcinogenic risk found for all measured metals in relation to ingestion and dermal contact, since the HQs and HI values are less than one, with exception of HI values for children ($1.70E+00$) for point S1 and ($1.07E+00$) for point S2 were greater than 1 through ingestion pathway. This high values of HI in children via ingestion is an indication that heavy metal pollution might pose high non-cancer health risk to children living within the area. The values of HQinh and HI ingestion and inhalation for all the heavy metals studied from both point S1 and S2 were much more greater than 1 (Table 15), which is an indication of high potential non-cancer related illness to children and adult within the study area. Results of HQ further indicates that, inhalation and HI ingestion is the main pathway of exposure of the studied heavy metals. Also, the values of hazard quotient (HQing) for the studied heavy metals for children and adults in both locations are in the order of $Pb > As > Cr > Hg > Cd > Cr > Ni$; $As > Cr > Cd > Ni$. $>Hg > Pb$ (HQinh) and $Cd > Cr > Ni > Pb > As > Hg$ (HQdermal). The results of HQ also demonstrated that, the values of various routs of exposure pathway for all the study heavy metals in children and adults are in the order of $inhalation > ingestion > dermal$ contact. Values for HQing and HQinh were higher in children than adults, which is a further indication that children are face with more potential non-cancer health risk through ingestion and inhalation of heavy metals in soil from the study locations. These results are similar with those reported by [8, 13, 29, 42, 43].

3.7.3 Cancer Risk (CR)

Results from cancer risk (CR) shows that values of metals with the available slop factors for inhalation and dermal contact ranged from $3.50E-08$ to $1.20E-05$ Table 16. The United State Environmental Protection Agency considers acceptable for regulatory purposes a cancer risk in the range of 1.0×10^{-6} to 1.0×10^{-4} [32]. The carcinogenic risks values for As, Pb and Ni through CRing and CRdermal contact for children and adult were lower than the said regulatory acceptable values of 1.0×10^{-6} to 1.0×10^{-4} [32], and showed no cancer risk to the population. However, values for CRinh for children and adult ranged from $2.23E-03$ to $8.10E-01$, and these ranged of values were relatively higher than the acceptable threshold values of 1.0×10^{-6} to 1.0×10^{-4} [32]. Therefore, As, Cd, Ni and Cr in soil through CRinh

Table 14: Average Daily Dose (ADD) Exposure Duration (mg/kg) Via Ingestion, Inhalation and dermal Contact for both Children and Adult

Metal	S ₁						S ₂					
	ADD _{ing}		ADD _{inh}		ADD _{dermal}		ADD _{ing}		ADD _{inh}		ADD _{dermal}	
	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult
Hg	1.75E-05	2.31E-06	4.50E-03	2.00E-03	2.8E-08	7.04E-08	2.86E-06	3.77E-07	7.35E-04	3.26E-04	4.57E-09	1.15E-08
As	6.35E-05	8.38E-06	1.63E-02	7.20E-03	1.0E-07	2.55E-07	3.98E-05	5.26E-06	1.00E-02	4.54E-03	6.37E-08	1.60E-07
Pb	4.81E-05	6.35E-06	1.24E-02	5.50E-03	7.7E-08	1.93E-07	3.12E-05	4.12E-06	8.04E-03	3.56E-03	5.00E-08	1.26E-07
Cd	2.71E-05	3.58E-06	7.00E-03	3.10E-03	4.3E-08	1.09E-07	2.04E-05	2.70E-06	5.50E-03	2.33E-03	3.27E-08	8.21E-08
Ni	3.87E-05	5.10E-06	9.90E-03	4.40E-03	6.2E-08	1.55E-07	2.34E-05	3.08E-06	6.01E-03	2.66E-03	3.74E-08	9.39E-08
Cr	6.99E-05	9.23E-06	1.80E-02	8.00E-03	1.1E-07	2.81E-07	5.38E-05	7.11E-06	1.40E-02	6.14E-03	8.61E-08	2.16E-07

S₁ = Zabarmari Agricultural Location
 S₂ = Bulamari Agricultural Location

Table 15: Non-carcinogenic Risk Values via Ingestion, Inhalation and dermal Contact for both Children and Adult

Metals	S ₁						S ₂					
	HQ _{ing}		HQ _{inh}		HQ _{dermal}		HQ _{ing}		HQ _{inh}		HQ _{dermal}	
	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult
Hg	5.83E-02	7.70E-03	1.50E+01	6.67E+00	9.33E-05	2.35E-04	9.53E-03	1.26E-03	2.45E+00	1.09E+00	1.52E-05	3.83E-05
As	2.12E-01	2.79E-02	1.09E+03	4.80E+02	1.11E-04	2.83E-04	1.33E-01	1.75E-02	6.67E+02	3.03E+02	7.08E-05	1.78E-04
Pb	1.37E+00	1.81E-01	3.54E+00	1.57E+00	1.48E-04	3.71E-04	8.91E-01	1.18E-01	2.30E+00	1.02E+00	9.62E-05	2.42E-04
Cd	2.71E-02	3.58E-03	4.67E+02	2.07E+02	4.30E-03	1.09E-02	2.04E-02	2.70E-03	3.67E+02	1.55E+02	3.27E-03	8.21E-03
Ni	1.94E-03	2.55E-04	1.10E+02	4.89E+01	6.89E-04	1.72E-03	1.17E-03	1.54E-04	6.68E+01	2.96E+01	4.16E-04	1.04E-03
Cr	2.33E-02	3.08E-03	6.29E+02	2.80E+02	1.83E-03	4.68E-03	1.79E-02	2.37E-03	4.90E+02	2.15E+02	1.44E-03	3.60E-03
HI	1.70E+00	2.24E-01	2.31E+03	1.02E+03	7.17E-03	1.82E-02	1.07E+00	1.42E-01	1.59E+03	7.04E+02	5.30E-03	1.33E-02

Table 16: Cancer Risk Values of Heavy Metals for Adults and Children in soil Through Ingestion, Inhalation and Dermal Contact

Metals	S ₁						S ₂					
	CR _{ing}		CR _{inh}		CR _{dermal}		CR _{ing}		CR _{inh}		CR _{dermal}	
	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult
Hg	-	-	-	-	-	-	-	-	-	-	-	-
As	9.53E-05	1.26E-05	2.50E-01	1.09E-01	3.66E-07	9.33E-07	5.97E-05	7.89E-06	1.51E-01	6.86E-02	2.33E-07	5.86E-07
Pb	4.09E-07	5.4E-08	-	-	-	-	2.65E-07	3.50E-08	-	-	-	-
Cd	-	-	4.41E-01	1.95E-02	-	-	-	-	3.47E-02	1.47E-02	-	-
Ni	3.25E-05	4.28E-06	8.32E-03	3.70E-03	-	-	1.97E-05	2.59E-06	5.05E-03	2.23E-03	-	-
Cr	-	-	8.10E-01	3.60E-01	-	-	-	-	6.30E-01	2.67E-01	-	-

can induce possible cancer risk in both children and adults within the study areas. Values from CR assessment also revealed inhalation as the major possible route of exposure to excess lifetime cancer risk with children being more exposed to heavy metals in soil as compared to adults.

3.8 Risk Assessment of Heavy Metals in Rice

Results of average daily dose (ADD) of the studied heavy metals in different varieties of rice samples from point S1 and S2 are as presented in Table 17. The observed ADD of Hg, As, Pb, Cd, Ni and Cr in the different

varieties of rice ranged from 7.83E-04 to 1.11E-03, 1.84E-03 to 4.19E-03, 1.10E-03 to 2.92E-03, 5.85E-04 to 1.39E-03, 4.95E-04 to 1.69E-03 and 6.84E-04 to 3.29E-03 mg/kg day-1 respectively. Comparing with the recommended safe values of Hg (0.57) by Joint FAO/WHO Expert Committee Food Additive (JECFA) [80], As (3.0) by [80], Pb (1.5) by [81], Cd (0.8) by [81], Ni (5.0) by [82] and Cr (5.0) by [82], the detected ADD values for all the studied metals were lower than the recommended safety limits. Similar studies as conducted by [52] reported different ADD values of As, Cd, Hg and Pb through rice are estimated to be 0.49, 0.23, 0.03 and

0.37 mg/kg bw/day respectively and [60] also reported higher ADD values for Pb, Cd and Cr through rice were estimated to be 4.02, 0.27 and 1.98 mg/kg/day respectively. Average daily intake values greater than the safe limits have also been reported by [54] through rice were estimated to be Ni, Pb, Cr, Cd, and Hg were 54, 279, 1050, 29, and 0.28 mg/kg/day respectively.

Results of ADD further indicate that consumption of rice from the two agricultural locations will not result in any health problems by exposure of the study metals. Hazard quotient (HQ) and hazard index (HI) of heavy metals are presented in Table 18. The health risks from consumption of contaminated rice by adult population were assessed based on Hazard Quotient (HQ) which is the ratio of determined dose level. If $HQ > 1$, the exposed population will have detrimental health effect [83]. Finding from the present study revealed that the values for HQ were less than one (1), which shows that there is no adverse health effect associated with metals through consumption of rice. However, the HQ value for As within the study locations were greater than one (1), this indicates a potential health risk associated with As through consumption of rice. Higher HQ values of Cd, Cr, As, and Pb were also reported by [16, 84] for Pb. The hazard index (HI) value expresses the combined non-carcinogenic effects of multiple elements for consumption of selected rice. Hazard index (HI) values of metals for all the varieties of rice ranged from $1.22E+00$ to $1.40E+01$. This ranged of values were above one (1), indicating high potential of non-cancer health risk via consumption of rice. Higher HI values in vegetables were also reported by [16, 85]. The high values of HI for all the heavy metals observed in the varieties of rice call for serious concern because of the high potential to pose health risk to the population that consume these varieties of rice.

4. Conclusion

The present study was carried out to assess the levels of heavy metals in soil and varieties of rice and their potential associated with health risk in Maiduguri. Generally, the concentrations of all the studied metals in the soil samples were significantly higher at a depth of 0-5 cm, while 10-15 cm showed the lowest. Narica 1 and Marica 2 varieties of rice were observed to accumulate higher concentrations of heavy metals than other varieties.

The concentrations of all the metal in the soil samples from both studied locations were lower than the WHO/FAO permissible limits, while values of various rice were all above the said WHO/FAO limits. Results from potential ecological risks assessment and the potential ecological risk factors (RI) shows that Cd had

very high potential ecological risk and dangerous to the environment and give course for concern, while Hg, As, Pb, Ni and Cr were relatively much less than 40 indicating low risk. Also, AEI results for all the metals were greater than 1, indicating a possibility of likelihood to induce adverse biological effects to benthic organism with exception to Hg and Cd. The geoaccumulation index results for all the metals were within the background values, with exception of Pb which is moderately polluted. The values of contamination factor (CF) shows that the soil samples were not contaminated by the studied heavy metals, with exception of Hg at point S1 with average value of 1.78 which was moderately contaminated. Results for pollution load index (PLI) revealed that the PLI values of As, Pb, Cd, Ni and Cr fell within the $PLI \leq 1$ category, indicating no pollution of the studied soil. The soil ADD values for both children and adult for ingestion and dermal contact were lower than their individual RfDs, which shows that both children and adult population are not under any threat from non-carcinogenic risk as a result of metal contamination. But values via inhalation for both children and adult were higher than the RfDs values, indicating ADD_{inh} as the most dominant pathway for the exposure of metals to both children and adult population. For rice samples, the observed dietary intake values of the six studied metals were less than JECFA permissible safety limits. Results of HQ and HI for all the heavy metals were less than the safe limit of 1 for ingestion and dermal pathways, with exception of HI values for children ($1.70E+00$) for point S1 and ($1.07E+00$) for point S2 which were greater than 1 due to ingestion pathway, signifying high potential non-cancer health risk to children. The values of HQ_{inh} and HI_{inh} for all the heavy metals for both point S1 and S2 were much greater than 1, an indication of high potential non-cancer related illness to children and adult, signifying inhalation and HI_{ingest} as the main pathway of exposure of the studied heavy metals for children and adult. The carcinogenic risks values for As, Pb and Ni through CR_{ing} and CR_{dermal} contact for children and adult were lower than the said regulatory acceptable values of 1.0×10^{-6} to 1.0×10^{-4} , which shows non-cancer risk. However, values for CR_{inh} for children and adult ranged from $2.23E-03$ to $8.10E-01$, and these ranged of values were relatively higher than the acceptable threshold values of 1.0×10^{-6} to 1.0×10^{-4} , showing possibility of inducing non-cancer risk in both children and adults. The main exposure pathway for both children and adults is inhalation, followed by ingestion and dermal contact. For the rice samples, the observed dietary intake values of each of the metals were less than JECFA recommended safety limits, and hazard quotients values are also less than the US EPA permissible safety limit of 1, which signify no health risk of the heavy metal exposure through the consumption of the varieties of rice. HQ value for As and HI values for all the studied metals

Table 17: Average Daily Dose of Some Heavy Metals in Varieties of Rice

Samples	S1						S2					
	Daily Dose (mg/kg day-1)						Daily Dose (mg/kg day-1)					
	Hg	As	Pb	Cd	Ni	Cr	Hg	As	Pb	Cd	Ni	Cr
Narica 1	1.11E-03	4.19E-03	2.92E-03	1.39E-03	1.69E-03	3.29E-03	2.43E-04	1.68E-03	1.93E-03	1.12E-03	8.82E-04	2.89E-03
Marica 2	9.63E-04	2.92E-03	2.48E-03	7.83E-04	4.95E-04	1.51E-03	9.90E-05	1.41E-03	9.54E-04	9.63E-04	5.04E-04	1.92E-03
De-gold	7.83E-04	1.84E-03	1.10E-03	6.84E-04	1.39E-03	1.22E-03	7.20E-05	1.19E-03	1.99E-03	8.64E-04	7.38E-04	1.28E-03
Faro 44	1.01E-03	2.68E-03	2.49E-03	5.85E-04	8.46E-04	6.84E-04	5.40E-05	1.49E-03	1.60E-03	7.92E-04	5.76E-04	5.31E-04
TDD	3.86E-03	1.16E-02	8.98E-03	3.44E-03	4.42E-03	6.71E-03	4.68E-04	5.78E-03	6.47E-03	3.74E-03	2.70E-03	6.62E-03

S₁ = Zabarmari Agricultural Location

S₂ = Bulamari Agricultural Location

were greater than one (1), indicating high potential of

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Table 18: Hazard Quotient and Hazard Index of Some Heavy Metals in Varieties of Rice

Samples	S1						S2					
	HQ (mg/kg day-1)						HQ (mg/kg day-1)					
	As	Pb	Cd	Ni	Cr	HI	As	Pb	Cd	Ni	Cr	HI
Narica 1	1.40E+01	7.29E-01	1.39E+00	8.46E-02	2.19E-03	1.62E+01	1.12E-03	4.82E-01	1.12E+00	4.41E-02	1.93E-03	1.65E+00
Marica 2	9.72E+00	6.19E-01	7.83E-01	2.48E-02	1.01E-03	1.11E+01	9.42E-04	2.39E-01	9.63E-01	2.52E-02	1.28E-03	1.23E+00
De-gold	6.12E+00	2.75E-01	6.84E-01	6.93E-02	8.16E-04	7.15E+00	7.92E-04	4.97E-01	8.64E-01	3.69E-02	8.52E-04	1.40E+00
Faro 44	8.94E+00	6.23E-01	5.85E-01	4.23E-02	4.56E-04	1.02E+01	9.96E-04	4.01E-01	7.92E-01	2.88E-02	3.54E-04	1.22E+00

cancer health risk via consumption of rice. Since values from this research shows that some metals have potential to course carcinogenic and non-carcinogenic health risk, we therefore, recommend regular monitoring of heavy metal in soil and varieties of rice within the study locations in other to protect human health.

Conflict of Interest

The authors declare that they have no conflict of interest.

Acknowledgment

Authors gratefully thank the full financial support from TetFund (Tertiary Educational Trust Fund, Nigeria) through University of Maiduguri Management (Tetfund/DESS/UNI/ MAIDUGURI/RP/VOL.V).

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