

Comparative Evaluation of Speciation of Heavy Metals in Irrigation Farm of Railway Quarters, Bauchi Metropolis, Bauchi State, Nigeria

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Abstract: Untreated water is widely used for irrigation in water scarce regions in several States of Nigeria including Bauchi State. The nutrients contained in the wastewater are considered as beneficial to agriculture, the contaminants present in it can pose environmental and health risk. Irrigated farms could be used to improve the food productivity in the country. The concentrations of heavy metals (Cd, Cr, Cu, Mn, Ni and Pb) in irrigation and non-irrigation soils of Railway Quarters, Bauchi were analysed using fractionation methods and determined using Atomic Absorption Spectrophotometry. In the exchangeable bound fraction, the results revealed the highest concentrations (mg/kg) of Cd (0.22), Cu (60.00) and Mn (33.00) in the irrigation soil, whilst those of Cu (20.00) and Cd (0.33) in non-irrigation soil. The highest concentrations (mg/kg) in the residual bound fraction was observed in Cr, Ni and Pb in the irrigation soil, as well as Cr, Mn, Ni and Pb in non-irrigation soil. The fractional sum of all the metals in the six fractions (exchangeable, carbonate, manganese oxide, iron-manganese, organic matter sulphide and residual) were found to be (mg/kg): lead (29.00), copper (298.00), cadmium (0.66), chromium (11.00), manganese (167.00) and nickel (72.00). The results revealed that all the observed concentrations are within the permissible limits of DPR (2002) and WHO/FAO (2001) with the exception of that of copper and nickel. The non-irrigation soil showed the cumulative sum of the levels (mg/kg) of the heavy metals in the six fractions: Pb (10.00), Cu (44.30), Cd (0.36), Cr (5.65), Mn (67.27) and Ni (6.00) are within the threshold levels of WHO/FAO (2001) and DPR (2002) respectively. The observed values to some extent do not pose health threat to the inhabitants and consumers.

I. INTRODUCTION

Among the challenges that is facing the production of food via irrigation presently is the adulteration of soil and water [1]. Soil is a habitat for a great number of organisms and is the main part of terrestrial ecosystem. It is the most endangered component of our environment that is exposed to effluents from many pollutants arising from anthropogenic activities [2]. Heavy metals get into our environment from both natural and anthropogenic sources, adulterated food sources and increase in mass in both agricultural products and sea food via air, soil and water [3]. When heavy metals are added to the soil, they may affect microbial proliferation and enzymatic activities thereby leading to reduction in the rates

of the biochemical processes in soil environment. The pollution of environment with heavy metals arises as a result of increase in the level of industrialization and urbanization [4]. Unlike organic contaminants that are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo chemical or microbial degradation and their total concentration in soil persists for a long time after they have been introduced [5]. The availability of heavy metals in the environment above permissible levels requires attention due to their harmful effects [6]. The entering of poisonous and noxious heavy metals into the ecosystem may result to geo-accumulation, bio-magnifications and bio-accumulation. Such metals become amassed instantly in soils, plants and would have a negative impact on the physiological activities of plants which include gaseous exchange, nutrient absorption and photosynthesis resulting in decrease in the growth of plants as well as dry matter accumulation and yield [7]. Extravagant collection of heavy metals in soils used for agriculture always leads to environmental contamination and raises heavy metal absorption by crops which also have impact on food quality and safety. Pesticides, fertilizers and manure are pollutants from agrochemical sources. One of the causes of increased neurological problem is as a result of consumption of food and vegetables contaminated with heavy metals [8].

Soil is not the only major nutrient-bearing environment for plant life, but it is also a supplier of various pollutants to plants due to the fact that plants can take up poisonous substances via their roots from soils. Heavy metals are extremely persistent in the environment; they are non-biodegradable and non-thermo degradable and therefore readily accumulate up to harmful and venomous concentrations. Heavy metals can accumulate in the soil at toxic levels due to long term application of wastewater [9]. Monitoring the adulteration of soil with heavy metals is important because of their influence on surface water, ground water as well as on plants, animals and humans. Irrigation using wastewater, application of agricultural fertilizers, organic manure, pesticides, industrial wastes disposal including urban wastes, atmospheric pollution from motor

vehicles and the combustion of fossil fuels are the major sources of heavy metals in agricultural soils [10]. The aim of this research work is to carry out comparative evaluation of speciation of heavy metals in irrigation farm of Railway Quarters, Bauchi Metropolis, Bauchi State, Nigeria.

II. MATERIALS

Buck Scientific Atomic Absorption Spectrophotometer Model 210 VGP and Orbital Shaker SOI were used for this research work. Chemicals of analytical reagent (AnalR) grade purity were also used in this study without further purification.

Description of the Study Area

Bauchi State is in North-East geo-political zone of Nigeria and was created in 1976. The State is located between latitudes $9^{\circ} 30'$ and $12^{\circ} 30'$ North of equator and between longitudes $8^{\circ} 45'$ and $11^{\circ} 0'$ East of the Green Wich Meridian. There are 20 Local Government Areas in the State namely: Alkali, Bauchi, Bogoro, Dambam, Darazo, Dass, Gamawa, Ganjuwa, Giade, Itas-Gadua, Katagum, Kirfi, Jama'are, Misau, Ningi, Shira, Tafawa Balewa, Toro, Warji and Zaki respectively (en.m.wikipedia.org/wiki/Bauchi-State). Railway Quarters is located between latitudes $10^{\circ} 17' 44.8''$ N and longitudes $9^{\circ} 51' 02.4''$ E.

Sampling and Sample pre-treatment

Bulk irrigation soil samples were collected randomly at a depth of 0-30 cm from different locations in the irrigation farm, as well as from the non-irrigation soil samples (control) along Railway Quarters, Bauchi. Soil samples of irrigation farm were homogenised separately to form a composite soil sample, air-dried, ground using a wooden pestle and mortar, sieved through a 2 mm mesh in order to remove the "not-soil and impurities". The sieved soil samples were stored separately in plastic bottles and labelled appropriately prior to laboratory analyses. The same method of pre-treatment was also carried out for the non-irrigation soil sample (control).

Fractionation / Partitioning of Heavy Metals

The concentrations of the heavy metals in various fractions were assayed in irrigation soil and non – irrigated (control) soil along Railway Quarters, Bauchi using the method adopted by Hassan *et al.*, 2019 [11] and classified into the fractions:

Fractions	Symbols
Exchangeable	F1
Carbonate	F2
Manganese Oxide	F3
Iron – Manganese Oxide	F4
Organic Matter Sulphide	F5
Residual	F6

III. METHODS

Determination of Exchangeable Bound Metals

A 1.00 g of the soil sample (irrigated and non-irrigated) were respectively weighed into two different 250 cm³ conical flasks and 10.00 cm³ of 1.00 mol/dm³ sodium ethanoate solution were individually added to the two flasks. The pH of the two mixtures was separately adjusted to 8.7 by the addition of 1.00 eq/dm³ of sodium hydroxide solution. The mixtures were agitated for 2 hours using Orbital Shaker Model SOI, filtered into two different 100 cm³ volumetric flasks using Whatman Filter Paper Number 1. The filtrates were made up to the mark with water. The metals were determined using Atomic Absorption Spectrophotometer (AAS) and the residues were reserved for further fractionation [11].

Determination of Carbonate Bound Metals

The residues from the exchangeable bound metals were leached each for 3 hours with sodium ethanoate solution and the pH adjusted to 5.00 using ethanoic acid. The leachates were transferred into two different 100 cm³ volumetric flasks and made up to the desired volume with water. The leachates were analysed for metals of interest using AAS and the soil residues were reserved for further analyses [11].

Determination of Manganese Oxide Bound Metals

The residues from the carbonate bound soils were leached each with 10.00 cm³ of 0.10 mol/dm³ hydroxylamine hydrochloride solution and 0.01 mol/dm³ trioxonitrate (V) acid added. The mixture was agitated for three (3) hours using an Orbital Shaker SOI and the pH adjusted to 2.00 by the addition of ethanoic acid. The leachates were quantitatively transferred into two different 100 cm³ volumetric flasks and made up to the mark with water. The leachates were used to analyse metals of interest using AAS and the residues were reserved for further determinations [11].

Determination of Iron-Manganese Oxide Bound Metals

The residues from the manganese oxide bound soils were extracted each using 10.00 cm³ of pH 3 oxalate buffer after shaking for 12 hours at 90°C in a water bath. The extracts were filtered into two different 100 cm³ volumetric flasks and water was added to mark. The extracts were also analysed for metals of interest using Atomic Absorption Spectrophotometer (AAS) Model 210 VGP and the residues were kept for further fractionation and analyses [11].

Determination of Organic Matter-Sulphide Bound Metals

The separate residues from the iron-manganese oxide bound soil were each extracted by agitating in the presence of 10.00 cm³ of 30.00 % hydrogen peroxide. The pH was adjusted to 2.00 by the drop-wise addition of trioxonitrate (V) acid, heated at 90°C in a water bath for six (6) hours and filtered into a 100 cm³ volumetric flask. Further re-extraction was carried out at room temperature using 10.00 cm³ of 1.00 mol/dm³ aqueous ammonium ethanoate that was adjusted to a

pH of 2.00, agitated for three (3) hours, filtered into the first extract that was initially in two separate 100 cm³ volumetric flask and water added to capacity. The solutions (sample and control) were used to determine the metals of interest using AAS. The residues were kept for further fractionation and analyses [11].

Determination of Residual Metals

The soil residues from the organic matter sulphide bound soil (for both the sample and control) were digested each with 10.00 cm³ of aqua-regia by heating in a digestion tube at a temperature of 250⁰C. The clear digests were respectively decanted, cooled and transferred quantitatively into two separate 100 cm³ volumetric flasks and made to volume with water. The solutions were then analysed for the metals of interest using AAS at their respective wavelengths [11].

Geo-accumulation Index (GAI)

Geo-accumulation Index (GAI) was used to evaluate the levels of metal adulteration in irrigation and non-irrigation soil samples. The geo-accumulation index was calculated using the formula:

$$GAI = \log 2 C_n / 1.5 B_n,$$

where C_n is the concentration of elements in the enriched sample, B_n is the geochemical background concentration for the same elements and 1.5 is the background matrix correction factor due to lithological variations [12]. In this study, the concentrations (mg/kg) of heavy metals in irrigation soil were used as C_n (Cr: 11.00, Mn: 167.00, Ni: 72.00, Pb: 29.00, Cu: 298.00 and Cd: 0.66) while the levels of heavy metals in non-irrigation (control) soil were also used as B_n: (Cu: 44.30, Mn: 67.27, Ni: 6.00, Pb: 10.00, Cr: 5.65 and Cd: 0.36). The geo-accumulation index is classified into seven factors: uncontaminated (GAI = 0), uncontaminated to moderately contaminated (0 < GAI < 1), moderately contaminated (1 < GAI < 2), moderately to strongly contaminated (2 < GAI < 3), strongly contaminated (3 < GAI < 4), strongly to extremely contaminated (4 < GAI < 5) and extremely contaminated (GAI > 5).

Quality Assurance

Chemicals used were of analytical grades and distilled water was used in the preparation of all the solutions. The glass wares used were thoroughly washed with detergent solution, repeatedly rinsed with water and the solution used in them. The mixture of all the reagents used (without the samples) were used to auto-zero the machine. Precisions and accuracy of the results were monitored through repeated determinations.

IV. RESULTS AND DISCUSSION

Results

Table 1 shows the levels (mg/kg) of cadmium, chromium and copper in fractionated irrigation soil sample of Railway Quarters, Bauchi, while Table 2 indicates the concentrations

(mg/kg) of manganese, nickel and lead in the fractionated irrigation soil sample of the same Railway Quarters, Bauchi. Table 3 reveals the levels (mg/kg) of cadmium, chromium and copper in fractionated non-irrigation soil sample (control) of Railway Quarters, Bauchi, whilst Table 4 depicts the concentrations (mg/kg) of manganese, nickel and lead in fractionated non-irrigation soil sample (control) of Railway Quarters, Bauchi. Table 5 indicates the values of Geo - accumulation Index (GAI) of the analysed heavy metals.

Table 1: Levels of Cadmium, Chromium and Copper (mg/kg) in Different Fractions in Irrigation Farm of Railway Quarters, Bauchi

Fractions	Cd	Cr	Cu
F1	0.22 ^b ± 0.01	1.00 ^f ± 0.01	60.00 ^a ± 0.00
F2	0.22 ^b ± 0.01	1.00 ^e ± 0.00	57.00 ^a ± 0.07
F3	ND	2.00 ^d ± 0.01	44.00 ^e ± 0.00
F4	0.22 ^b ± 0.00	2.00 ^c ± 0.00	45.00 ^e ± 0.00
F5	ND	2.00 ^b ± 0.00	45.00 ^e ± 0.00
F6	ND	3.00 ^a ± 0.00	47.00 ^b ± 0.00
Total	0.66	11.00	298.00

ND: Not Detected. Values are mean ± standard error of the mean (n = 3). Values on the same column with same superscript alphabets are significantly the same, while those with different superscript letters are statistically different (p ≤ 0.05) as revealed by one way ANOVA and least significant difference (LSD).

Table 2: Concentrations (mg/kg) of Some Heavy Metals (Manganese, Nickel and Lead) in Different Fractions of Irrigation Soil in Railway Quarters, Bauchi

Fractions	Mn	Ni	Pb
F1	33.00 ^a ± 0.00	10.00 ^a ± 0.00	3.00 ^d ± 0.00
F2	31.00 ^b ± 0.00	11.00 ^a ± 0.00	4.00 ^c ± 0.00
F3	29.00 ^c ± 0.01	12.00 ^a ± 0.00	4.00 ^c ± 0.00
F4	26.00 ^d ± 0.01	13.00 ^a ± 0.00	5.00 ^b ± 0.00
F5	25.00 ^e ± 0.01	13.00 ^a ± 0.00	6.00 ^a ± 0.00
F6	23.00 ^f ± 0.01	13.00 ^a ± 0.00	7.00 ^a ± 0.00
Total	167.00	72.00	29.00

Values are mean ± standard error of the mean (n = 3). Values on the same column with same superscript letters are significantly the same, whilst those with different superscript letters are statistically different (p ≤ 0.05) as revealed by one way ANOVA and least significant difference (LSD).

Table 3: Concentrations of Cadmium, Chromium and Copper in Non - irrigation (control) Soil of Railway Quarters, Bauchi

Fractions	Cd	Cr	Cu
F1	0.33 ^h ± 0.00	0.33 ^e ± 0.00	20.00 ^g ± 0.06
F2	ND	0.66 ^c ± 0.01	7.00 ^e ± 0.04
F3	0.03 ^h ± 0.00	0.66 ^c ± 0.01	4.30 ^e ± 0.02
F4	ND	1.00 ^c ± 0.00	6.00 ^e ± 0.15

F5	ND	1.33 ^c ± 0.01	4.00 ^e ± 0.03
F6	ND	1.67 ^c ± 0.01	3.00 ^e ± 0.03
Total	0.36	5.65	44.30

ND: Not Detected. Values are mean ± standard error of the mean (n = 3). Values on the same column with same superscript letters are significantly the same (p ≤ 0.05) as revealed by one way ANOVA.

Table 4: Levels of Manganese, Nickel and Lead in Non-irrigation (control) Soil of Railway Quarters, Bauchi

Fractions	Mn	Ni	Pb
F1	7.60 ^d ± 0.00	ND	1.00 ^f ± 0.01
F2	10.67 ^d ± 0.01	1.00 ^e ± 0.01	1.33 ^f ± 0.01
F3	11.00 ^d ± 0.01	1.33 ^e ± 0.01	1.67 ^f ± 0.01
F4	12.00 ^d ± 0.01	1.00 ^e ± 0.01	1.00 ^f ± 0.01
F5	12.00 ^d ± 0.01	0.67 ^e ± 0.01	2.00 ^f ± 0.01
F6	14.00 ^d ± 0.01	2.00 ^d ± 0.01	3.00 ^f ± 0.01
Total	67.27	6.00	10.00

ND: Not Detected. Values are mean ± standard error of the mean (n = 3). Values on the same column with the same superscript letters are significantly the same (p ≤ 0.05) as revealed by one way ANOVA.

Table 5: Geo – accumulation Index (GAI) of Heavy Metals

Heavy Metals	GAI
Cd	0.37
Cr	0.39
Cu	1.35
Mn	0.50
Ni	2.41
Pb	0.58

Discussion

Relative Distribution of Cadmium, Chromium and Copper in Fractionated Irrigation and Non-irrigation Soil Samples

Tables 1 and 3 indicate the levels (mg/kg) of cadmium, chromium and copper in irrigation and non – irrigation soil samples respectively in six fractions of exchangeable (F1), carbonate (F2), manganese oxide (F3), iron-manganese oxide (F4), organic matter sulphide (F5) and residual (F6) and their corresponding standard errors of the means as measures of precision.

The same concentrations of cadmium were found in the exchangeable, carbonate and iron-manganese oxide bound fractions (0.22 mg/kg) of the irrigation soil, while the levels of cadmium found in manganese oxide, organic matter sulphide and residual (F3, F5 and F6) were below detection limit. Cadmium (mg/kg) was only observed in the exchangeable bound (0.33) and manganese oxides bound fractions (0.03) of non – irrigation soil. The presence of cadmium in the soil may be due to disposal of wastewater from households. The

application of artificial phosphate fertilizers may also contribute to the presence of cadmium in the soil when wastes from fertilizers applied are dumped into the environment. Analysis of variance (ANOVA) indicated that there was no statistical significant difference in the concentrations of cadmium among the six fractions of irrigation soil. The overall levels of cadmium in the six fractions (0.66 mg/kg) in irrigation soil is lower than the concentration range of cadmium found (17.89 to 31.75 mg/kg) in irrigated soil samples of some selected locations along River Kaduna, Nigeria [13]. On the other hand, the cumulative sum of observed cadmium (0.66 mg/kg) in irrigation soil and that of non – irrigation soil (0.36 mg/kg) are below the permissible limits of 0.80 mg/kg [14] and 3.00 mg/kg [15]. The concentrations of chromium investigated as observed in irrigation soil was in the trend of residual > organic matter sulphide (iron-manganese oxide, manganese oxide) > carbonate bound metals (exchangeable). The same levels of chromium in manganese oxide, iron – manganese oxide and organic matter sulphide (2.00 mg/kg) as well as exchangeable and carbonate bound fractions (1.00 mg/kg) were obtained in the irrigation soil. Chromium showed the highest level (1.67 mg/kg) in the residual bound fraction and lowest in the exchangeable bound fraction (0.33 mg/kg) in the non – irrigation soil (control). The observed trend of chromium in non – irrigation soil was residual > organic matter sulphide > iron-manganese oxides > manganese oxide (carbonate) > exchangeable bound fractions. The same concentrations (0.66 mg/kg) were obtained in both carbonate and manganese oxide fractions of non – irrigation soil. The sum of all the concentrations of chromium in the six fractions (11.00 mg/kg) of irrigation soil is lower than the concentration of chromium (276.67 mg/kg) in soil irrigated with wastewater in the Skhirat Region of Morocco [16] as well as chromium (48.40 mg/kg) in irrigated soil collected from different areas of Colombo District, Sri Lanka [17]. The cumulative values of chromium in irrigation soil (11.00 mg/kg) and that of non – irrigation soil (5.65 mg/kg) of this study are less than the permissible limits of chromium (100.00 mg/kg) [14] as well as lower than 150.00 µg/g (mg/kg) European Union Standard reported by Singh *et al.*, 2010 [18]. One – Way Analysis of Variance revealed a statistical significant difference (p ≤ 0.05) in the mean values of chromium among the six fractions of irrigation soil. Chromium (III) is an important nutrient for humans and its deficiency may lead to heart problems, diabetes and disruptions of metabolisms. The uptake of too much of chromium (III) can cause skin rashes. Chromium enters the air, water and soil in the chromium (III) and chromium (VI) forms/states through natural processes and human activities such as manufacturing of steel, leather and textile.

Copper has the highest concentration (mg/kg) in the exchangeable bound fraction of irrigation soil (60.00) and non – irrigation soil (20.00). The least concentration in irrigation soil was found in the manganese oxide bound fraction (44.00 mg/kg) and that of non – irrigation soil was in residual fraction (3.00 mg/kg). The observed concentrations of copper

in the irrigation soil gave the trend exchangeable > carbonate > residual > organic matter sulphide (iron – manganese oxide) > manganese oxide bound metals and the values in iron – manganese oxide and organic matter sulphide are the same. The levels of copper in non-irrigation soil gave the trend exchangeable > carbonate > iron – manganese oxide > manganese oxide > organic matter sulphide > residual bound metals. The fractional sum of copper in the six fractions of irrigation soil (298.00 mg/kg) exceeded the permissible limits of 36.00 mg/kg [14] and 100.00 mg/kg [15]. The cumulative sum of copper in non – irrigation soil (44.30 mg/kg) is within the permissible limit of 100.00 mg/kg [15]. Single-factor analysis of variance indicated a statistical significant difference ($p \leq 0.05$) in the concentrations of copper among the six fractions. Copper may be present in soil due to disposal of copper – containing wastewater. It also enters the air via the release of the combustion of fossil fuels. It remains in the air for a long period of time, settles down when rain falls and resulted in the high concentration of copper in the soil. It may also be present in the soil by both natural sources (wind –blown dust and decaying vegetation) and human activities such as metal pollution, wood production and phosphate fertilizer production.

Relative Distribution of Manganese, Nickel and Lead in Fractionated Irrigation and Non – Irrigation (Control) Soil Samples

Tables 2 and 4 show the concentrations (mg/kg) of manganese, nickel and lead in all the six fractions (F1 to F6) in irrigation and non-irrigation soils of Railway Quarters, Bauchi.

Manganese was mostly associated with the exchangeable bound fraction of irrigation soil (33.00 mg/kg). The observed trend in the six fractions were exchangeable > carbonate > manganese oxide > iron- manganese oxide > organic matter sulphide > residual bound metals. The reverse is the case for non – irrigation soil. The highest concentration was observed in the residual, followed by organic matter sulphide (iron-manganese oxide), manganese oxide, carbonate and exchangeable fractions. The same concentrations were observed for both iron – manganese oxide and organic matter fractions. Similar result was obtained by Wufem *et al.*, 2009 [19] in which the concentration of manganese was found to be mostly bound to the residual fractions. One-Way Analysis of Variance showed a significant difference at 95.00 % confidence level in the levels of manganese among the six fractions of irrigation soil. In a research conducted by Muamar *et al.*, 2014 [16], concentration of manganese (81.76 mg/kg) is lower than the sum of all the fractional values of manganese (167.00 mg/kg) in irrigation soil and higher than that of non – irrigation soil (67.27 mg/kg). The fractional sums of manganese in all the soil samples are below the permissible limits of 850.00 mg/kg [14] and 2000.00 mg/kg in soils [15]. Irrigation with wastewater may lead to accumulation of heavy metals in the soil which can affect the soil flora and this may result in crop adulteration and low

yield. Manganese may be present in the soil as solids, small particles in water and dust particles in air through human activities such as burning of fossil fuels.

Nickel occurs mostly in the residual, organic matter sulphide and iron – manganese oxide bound fractions of irrigation soil (13.00 mg/kg). The statistical analysis (one-way ANOVA) revealed that there was no significant difference in the mean concentrations of nickel among the fractions. The observed trend in the six fractions of irrigation soil are F6 (F5, F4) > F3 > F2 > F1 in decreasing order of magnitude. In non-irrigation soil, the highest level of nickel was found in the residual fraction and the concentration observed in the exchangeable bound fraction was below detection limit. The summation of all the concentrations in the six fractions of irrigation soil (72.00 mg/kg) is lower than the Indian Standard safe limit (75.00 – 150.00 $\mu\text{g/g}$ or 75.00 – 150.00 mg/kg) of nickel in soil [18]. The cumulative sum of nickel in non – irrigation soil (6.00 mg/kg) is equally lower than the same Indian Standard safe limit of nickel. The presence of nickel in the soil can be attributed to both natural and anthropogenic sources.

Lead was mostly associated with the residual fractions of both irrigation (7.00 mg/kg) and non – irrigation (3.00 mg/kg) soils. The decreasing order of concentrations of lead in the irrigation soil was residual > organic matter sulphide > iron – manganese oxide > manganese oxide (carbonate) > exchangeable bound metals, while that of non-irrigation soil was residual > organic matter sulphide > manganese oxide > carbonate > exchangeable (iron – manganese oxide). The experimental results revealed the same values for carbonate and manganese oxide bound metals (4.00 mg/kg) in irrigation soil. The same values were also found in exchangeable and iron-manganese oxide bound metals (1.00 mg/kg) of non-irrigation soil. The fractional sum of lead concentrations (mg/kg) in irrigation (29.00) and non-irrigation soil (10.00) obtained in this study were lower than the concentration of lead (107.19 mg/kg) found in soil irrigated with wastewater in the Skhirat Region of Morocco [16] as well as the concentration range of lead (46.00 to 99.45 mg/kg) in irrigated soil samples of some selected locations along River Kaduna, Nigeria [13] and lead (39.70 mg/kg) in irrigated soils collected from different areas of Colombo Districts, Sri Lanka [17]. In addition, the concentrations of lead (mg/kg) in both irrigation (29.00) and non – irrigation (10.00) soils are below the permissible limits of 85.00 mg/kg [14] and 50.00 mg/kg in soil [15]. Single factor analysis of variance (ANOVA) indicated significant difference ($p \leq 0.05$) in the concentrations of lead among the six fractions of irrigation soil. The presence of lead in the environment may be due to the presence of lead pollutants in emissions from vehicles since lead is present in fuel as an anti-knocking agent. Lead can also enter drinking water through corrosion of pipes when the water is slightly acidic. Water flows from different houses through gutters and forms the irrigation wastewater which accumulates in the irrigation

soil and this can lead to higher concentrations when compared with non – irrigation soil.

Levels of Contamination Based on Geo-accumulation Index (GAI)

The results of geo-accumulation index of all the metals determined as indicated in Table 5 revealed that the metals have the following values: cadmium (0.37), chromium (0.39), copper (1.35), manganese (0.50), nickel (2.41) and lead (0.58). Based on the values, cadmium, chromium, manganese and lead are classified as uncontaminated to moderately contaminated, copper is moderately contaminated, while nickel is moderately to strongly contaminated.

V. DATA ANALYSES

Standard Error of the Mean

The standard error of the mean, a measure of precision of the observed values of the heavy metals in the study area were calculated, tabulated and presented in Tables 1 to 4. Precision is the closeness between several replicate determinations of the same parameter or quantity. The standard error of the means indicated good precision in all the replicate determinations of the observed values.

Single Factor ANOVA

The results of the heavy metals investigated in the study area were subjected to Single Factor or One – way ANOVA ($p \leq 0.05$). There were significant differences in the levels of the heavy metals based on fractionation or speciation (F1 to F6).

The Least Significant Difference Test

The least significant difference (LSD) was further carried in order to determine where the significant difference lie ($p \leq 0.05$). The extents of the significant differences are indicated in Tables 1 to 4.

VI. CONCLUSION

The study carried out on the heavy metals of interest revealed that Pb, Cr and Ni were mostly bound with the residual fractions in both irrigation and non – irrigation soil samples. Copper has the highest concentrations in all the fractions with a highest value of 298.00 mg/kg. The high level of lead observed in the residual fractions of both irrigation and non – irrigation could be traced to natural source (s). It therefore poses little to no effect in the environment because it is non-bio available as a result of its association mostly with the residual fractions. Partitioning of the metals in the soil also indicated higher levels of copper, cadmium and manganese in the exchangeable bound fractions. This shows the bioavailability of copper, cadmium and manganese in the irrigation soil which could be traced to their anthropogenic sources.

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