IJSRM
INTERNATIONAL JOURNAL OF SCIENCE AND RESEARCH METHODOLOGY
An Official Publication of Human Journals

Human Journals
Research Article
April 2018 Vol.:9, Issue:2
© All rights are reserved by A. U. Augustine et al.

Assessment of the Concentrations of Arsenic, Chromium and Nickel in Soils of an Irrigated Farmland of Lafia, Nasarawa State-Nigeria Using Nitric Acid and Aqua Regia Methods of Digestion

IJSRM
INTERNATIONAL JOURNAL OF SCIENCE AND RESEARCH METHODOLOGY
An Official Publication of Human Journals

A. U. Augustine[1*], T. M Akpomie[1], S. O. Osuagwu[1]

[1]Department of Chemistry, Federal University Lafia-Nigeria

Submission: 22 March 2018
Accepted: 29 March 2018
Published: 30 April 2018

HUMAN JOURNALS
www.ijsrm.humanjournals.com

Keywords: Arsenic, Chromium, Nickel, Aqua regia, Nitric Acid.

ABSTRACT

Washing of clothes, motorcycles and the release of smoke from vehicles and other anthropogenic sources continuously increase the levels of heavy metals in water bodies, especially the Amba river of Lafia used for the irrigation of farmlands thereby resulting to contamination and elevation of heavy metals uptake by crops. This research work was carried out to provide information on heavy metals concentration in soils of an irrigated vegetable farmland in Lafia. Soil samples were collected at surface levels of 0-30 cm depth. Samples were analyzed for pH, organic matter, electrical conductivity and clay content. The soil samples were digested using Aqua regia and Nitric acid methods of digestion. The concentrations of arsenic (As), chromium (Cr) and nickel (Ni) were determined by Atomic Absorption Spectrophotometric (AAS) technique. The values of soil pH ranged between 5.60 and 6.35, organic carbon between, 1.40-1.49 %, organic matter content between, 2.40 and 2.57 %, electrical conductivity between 100 and 240 µS cm^{-1} and clay, sand and silt content between 10.4-11.4 %, 82-85 % and 4.6-6.6 % respectively. Total concentration of extractable As, Cr, and Ni (Aqua regia method) ranged between 0.836–1.111, 0.316 –0. 444 and 0.061 – 0.157 mg kg^{-1} respectively. The concentration of heavy metals (Nitric acid method) were as follows: As: 0.206- 0.485, Cr: 0.260-0.375 and Ni: 0.091-0.264. Concentration of heavy metals in both methods were all below Tanzania and US EPA recommended limits. The results showed that aqua regia method was more efficient than the Nitric acid Method of digestion.

1.0 INTRODUCTION

Heavy metals are normally natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter human bodies *via* food, drinking water and air (Fergusson, 1990). Heavy metals are defined as elements in the periodic table having atomic number more than 20 or having densities more than 5 g/cm^3. The environmental burden with heavy metal are that they are non-degradable and most of them have toxic effect on living organisms when they exceeded a certain concentration level either in water, soil or food substances (Hong *et al.*, 2014).

Although some heavy metals like Cu, Fe, Mn, Zn are required for growth of plants in trace amounts, but prove fatal if present beyond their maximum permissible limits (Cai and Zhuang 1999; Freitas *et al.*, 2010; Nunes *et al.*, 2010). Various heavy metals *viz.*, arsenic, cadmium, copper, cobalt, lead, manganese, mercury, nickel and zinc are reported to cause genotoxicity upon reaching the living systems (Chandra *et al.*, 2005; Bertin and Averbeck 2006; Suciu *et al.*, 2008).

Arsenic is an element that raises much concern from both environmental and human health standpoints. Humans may encounter arsenic in water from wells drilled into arsenic-rich ground strata or in water contaminated by industrial or agrochemical waste (Young, 2006). They may come in contact with arsenic in contaminated dusts, fumes, or mists. They may eat food contaminated with arsenical pesticides or grown with arsenic-contaminated water or in arsenic-rich soil (Nriagu *et al.*, 1990).

Arsenic is found in the earth crust, mostly in form of iron arsenide sulfide (FeAsS). It can also be found in the atmosphere as arsenic trioxide dusts, a byproduct of industrial smelting operations. It is usually very toxic, especially in the cases of inorganic arsenic compounds such as arsenic trichloride and arsenous acid. Arsenic compounds have also found their way into rivers and wells, contaminating the drinking water of millions of people due to number of reactions that occurs with is, this element can be encountered in various phases (Meller, 1912; Young, 2006).

As (V) is dominant in aerobic environment, usually it is present in the form of (AsO_4^{3-},) in different protonation states $H_2AsO_4^-$, AsO_4^{3-}, H_3AsO_4, $H_2AsO_4^-$ (Bodek *et al.*, 1988). Mostly, arsenic present in the form of anion, with simple anions like SO_4^{2-} and Cl^- does not form complexes. Arsenic is associated to increase risk of cancer, skin damage and circulatory

system problems (Scragg, 2006).Arsenic mobility is enhanced by addition of phosphorus (Peryea and Kammereck, 1997). Arsenic is more mobile compared to lead regardless of the soil type and texture (Eflving *et al*., 1994).

Nickel is essential in small amount, but at high concentration (above tolerable levels), dangerous to health. Nickel can cause different types of cancer in various sites within animal's bodies, mainly those which live near refineries. The most common application of Ni is an ingredient of steel and other metal products. The important source of Ni contamination in the soil are electroplating, nickel mining, combustion of fossil fuels and metal plating industries (DPR-EGASPIN, 2002; Khodadoust *et al.*, 2004). Nickel also suffers the growth of microorganism but in the presence of it, microorganism usually develops resistance. It is not known that nickel are accumulating in plant and animal body and it has not been found that nickel biomagnify up food chain (Wuana and Okeimen., 2011). Ni has been reported to cause nasal and lung cancer (Li *et al*., 2013).

In nature chromium exist in two different oxidation states; trivalent (Cr^{VI}) and hexavalent (Cr^{III}) chromium. Both Cr^{III} and Cr^{VI} differ in terms of their mobility, toxicity and bioavailability. Cr^{VI} is found to be more toxic than Cr^{III} (Panda and Patra, 1997). Cr^{VI} forms chromate and dichromate which is highly soluble in water while Cr^{III} is less soluble in water and is required in trace amount as an inorganic nutrient for animals. Both chromate and dichromate are considered to be negatively charged and there is limited chance of it being adsorbed by organic materials. Cr^{VI} is considered to be more mobile than Cr^{III}. Thus Cr is extensively used in both the trivalent and divalent form in industries like steel, leather, textile etc (Dixit *et al.*, 2002).

Chromium phytotoxicity can result in inhibition of seed germination, degrade pigment status; nutrient balance oxidant enzymes and induce oxidative stress in plants (poschendrieder *et al.*, 1991; Barcelo and Poschenrieder 1997; Panda and Patra, 1997; Panda *et al.*, 2003; panda, 2003). Cr can also alter chloroplast and membrane ultrastructure in plants (Bassi *et al.*, 1990; Choudhury and Panda, 2004).

Chromium (Cr) is considered as a serious environmental pollutant, due to its wide industrial applications. Contamination of soil and water by Cr^{3+} is of recent concern. The Cr^{6+} compounds are used in industry for metal plating, cooling water treatment, hide tanning, and until recently, wood preservation (Nriagu, 1990). These anthropogenic activities have led to

the widespread contamination that Cr shows in the environment and have increased its bioavailability and biomobility (Kotas and Stasicka, 2000).chromium is remarkable for its magnetic properties, as it is the only elemental solid which shows antiferromagnetic ordering at room temperature (and below). Above 38ºC, it changes to paramagnetic (Fawcett, 1988). Chromium (VI) is carcinogenic and can lead to nasal septum perforation, asthma and liver damage (Scragg, 2006).

In recent studies carried out in southern Nigeria to evaluate the concentration level of heavy metals in soils of some arable farmland. The concentrations of Lead (Pb), Cadmium (Cd), Zinc (Zn) and Copper (Cu) were measured using flame atomic absorption spectrophotometer (FAAS). The concentration of Zn ranged from 12.98 to 38.94 µg/g and was the highest amongst the measured heavy metals. This was followed by Cu, 6.17 to 20.87 µg/g and then Pb, 0.79 to 8.35 µg/g, while the concentration of Cd, 0.26 to 5.75 µg/g was the least. Geostatistical analysis on the concentrations of the measured heavy metals revealed a significant ($p < 0.05$) spatial correlation (γ) with the soil pH and Organic Carbon (OC) (Pb, $\gamma = 0.74$; Cd, $\gamma = 0.67$; Zn $\gamma = 0.57$; Cu, $\gamma = 0.52$) and (Cd, $\gamma = 0.79$; Zn $\gamma = 0.59$; Cu $\gamma = 0.51$), respectively. The OC levels predispose soils to the retention of soil heavy metals and micro/macro-nutrients depending on the nature of OC-metal interaction. The concentrations of the heavy metals were below the European Economic Community (EEC) Maximum Allowable Concentrations (MACs) in agricultural soils, except for Cd. About 56% of the farmland soils contained more than 3 mg/kg of Cd, while about 44% were within the 1 to 3 µg/g EEC MAC for Cd in agricultural soils. Although the concentration levels of the measured heavy metals in the soils do not appear to be of serious concern, the study results provides evidence of gradual accumulation of Cd in farmlands (Olatunde *et al.*, 2013).

A study was carried out on heavy metal contamination on agricultural soils and water in Dares Salaam City, Tanzania, where heavy metals in soil and water were determined at four points along Msimbazi river valley in Dares Salaam city, which is popular for vegetable farming. Results indicated that the concentration of chromium in water ranged from (1.414±0.922) to 0.01 mg/L. Maximum and minimum lead concentrations of 0.113 and 0.083 mg/L were detected. The concentration of copper was generally low at all sites, ranging from (0.013±0.005) to (0.016±0.005) mg/L. The concentration of lead in water throughout the river exceeds the WHO (2004) drinking water limit of 0.01 mg/L, ranging from (0.113±0.104) to (0.083±0.059) mg/L. Cadmium concentration at all sampling points was

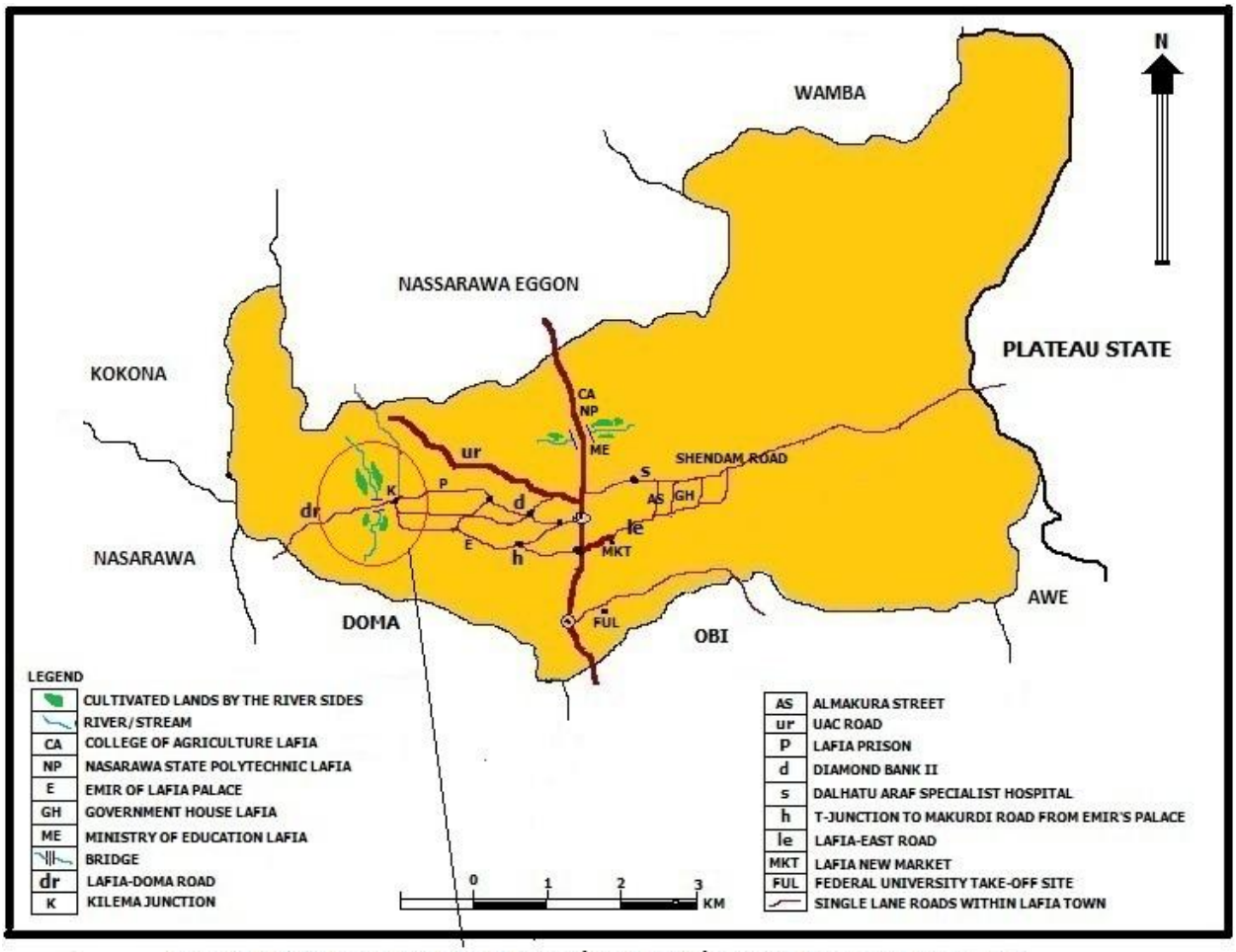
below detection limit of 0.01 mg/L. Soil analysis indicated that the concentrations of heavy metals are highest at the topsoil and decreased with depth. Lead had the highest concentration of (22.85±1.502) mg/kg; which did not exceed the TZS (2003) maximum limit of 200 mg/kg for soils. Chromium had maximum and minimum concentrations of (502.33±150.991) and (174.707±168.278) mg/kg, respectively, with most of samples exceeding the TZS (2003) permissible limit of 200 mg/kg. The maximum and minimum concentrations of copper were 21.073±2.881) and (4.513±1.713) mg/kg, respectively, lower than the TZS (2003) permissible limit of 100 mg/kg. Cadmium concentrations at all sampling points were lower than the permissible concentration of 100 mg/kg in soils (TZS, 2003). The presence of heavy metals in soil and water indicates the potential for pollution transfer from these media to the food chain, especially since this valley is popular for vegetable cultivation (Mwegoha and Kihampa, 2010).

This study aimed at assessing the concentrations of heavy metals (arsenic, chromium and nickel) and to determine the most important soil factors (chemical and physical) which influence heavy metals concentrations in soils of an irrigated farmland in Lafia, Nassarawa State, Nigeria.

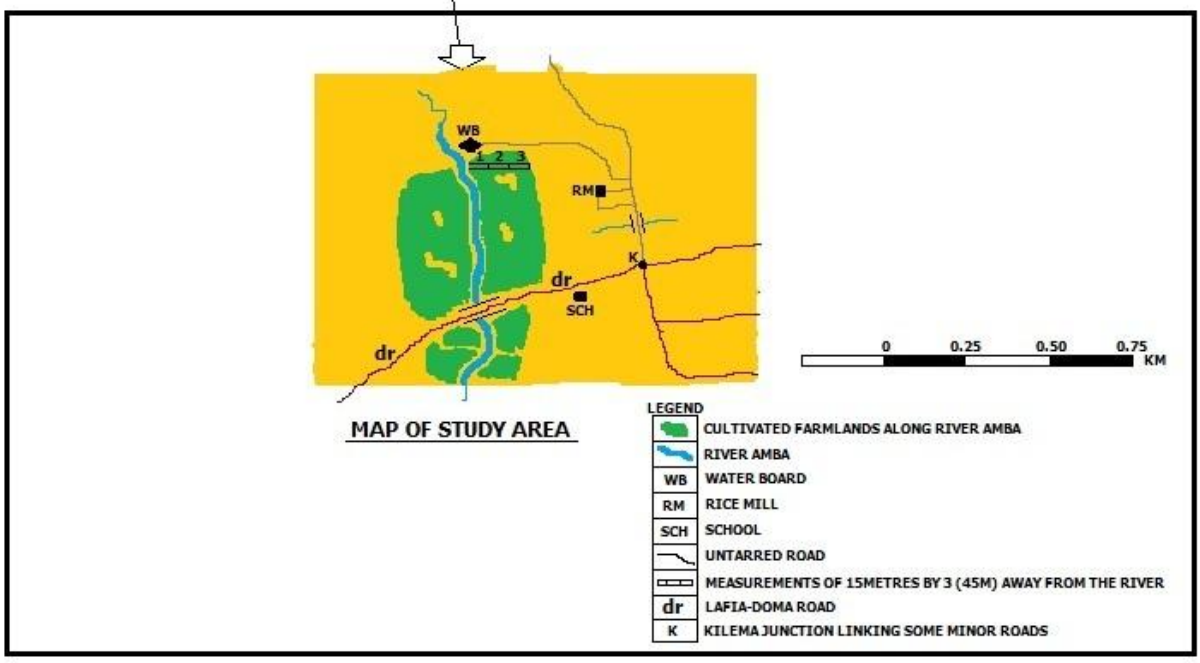
2.0 MATERIALS AND METHODS

2.1 Description of the Study Area

Lafia is the state capital and also a Local Government Area (LGA) in Nasarawa state. It has a Tropical climate with an average annual temperature and rainfall of 34.2 ^{0}C and 108 mm respectively. The highest amount of precipitation occurs around August with an average of 344.8 mm. the highest average temperature of 38^{0}C occurs between March and April. The minimum average temperature of about 19.3^{0}C occurs around December. The variation in temperatures throughout the year is 5.9^{0}C (NEITI, 2013).



MAP OF LAFIA SHOWING RIVER AMBA/RICE MILL/KILEMA AND SOME FEATURES



MAP OF STUDY AREA

2.2 Reagents/Apparatus used

All the chemicals used for this work were of analytical grades obtained from British Drug House (BDH) England. Doubly distilled water was used throughout the work. All glass wares used were soaked in 10% HNO_3 overnight and then washed with detergent, thoroughly rinsed with tap water and then with doubly distilled water.

2.3 Sampling, Sample Collection and Sample Preparation

The research was carried out on soil samples collected from irrigated farmland in Tundun Amba close to the intake of the state water board in Lafia metropolis between the months of February and March 2016. Soil samples were collected randomly at the sampling point. Three subsamples from the top layer were collected at a depth of 0-30 cm at a distance of 15 m each using a stainless steel auger and a measuring tape. The collected samples at each distance (0-15, 15-30 and 30-45 m,) make up three representative sample of the farmland. The samples were then pooled together to form a homogenous composite samples for the farmland. River Amba, the source of water used for the irrigation is close to the farmland. The samples were collected in a clean polythene bag, labeled and transported to the laboratory for further processing (Umar, 2013). The samples were designated as follows: sample A (0-15 m), sample B (15-30 m) and sample C (30-45 m).

2.4 Sample pre-treatment

The homogenized soil sample was air-dried in the laboratory for a week to avoid possible effect of sunlight on the sample, pounded in a clean mortar and pestle, after which it was pulverized and passed through a 2.0 mm alumina mesh sieve, then preserved in washed clean plastic bottles for analysis. This is for pH and total metal while for organic matter, some portion of the sieved soil sample was further pulverized to fine powder and passed through 0.5 mm sieve (Umar, 2013).

2.5 Determination of Soil pH

A 10.0 g of the soil sample was weighed into two different 100.0 mL beaker. A 25.0 mL of distilled water was added for pH in water, in one of the beakers and 25.0 mL of 0.01N Calcium chloride ($CaCl_2$) was added in the second beaker, the suspension was allowed to stand for 30 minutes and stirring occasionally with a glass stirring rod. This was to allow the

soil aggregate to break down so that the solution can equilibrate with the atmospheric oxygen. The pH of the soil was read using a pH meter (Luca and Nichola, 2012).

2.6 Determination of Organic Carbon and Organic Matter

A 1.0 g of the prepared sample was weighed into a 250.0 mL conical flask, followed by 10.0 mL of 1N potassium dichromate ($K_2Cr_2O_7$) and swirled gently to disperse the soil. A 20.0 mL of concentrated sulfuric acid (H_2SO_4) was added using a measuring cylinder directing the stream into the suspension and swirled immediately until the reagents are mixed, swirled more vigorously for one minute and allowed the suspension to stand for 30 minutes, followed by 100.0 mL of distilled water after standing for 30 minute, then 3 drops of indicator (Barium diphenyl sulphonate ($Ba(C_6H_5)_2SO_2$) was added, and titrated with 0.5 N ferrous sulphate solution. As the endpoint is approached, the solution takes on a greenish cast and then changed to dark green. At this point, ferrous sulphate was added drop by drop until the colour changed sharply from blue to red (maroon color) in reflected light against a white background. The blank titration was done following same procedure but without the soil sample and the result calculated! (Walkly and Black, 1934).

Calculation: $$\%OC = \frac{(Me\ K_2Cr_2O_7 - Me\ FeSO_4 \times 0.3 \times f}{Of\ soil\ (g)} \times 100$$

Where:

Correction factor F= 1.33, M = Normality of solution x ml of solution used.

Organic Matter (OM) calculated from the result of organic carbon multiply by a constant

$$\%OM = \%\ OC \times 1.72$$

2.7 Determination of Electrical Conductivity (EC)

A 50.0 g of the soil was weighed and dissolved in 100.0 mL of distilled water of a 250.0 mL glass beaker, the mixture was stirred gently for 30 seconds and allowed to stand for 30 minutes. The solution was stirred gently again before taking the EC reading. The EC meter was inserted into the soil and swirled round gently in the soil-water extract. After 30 seconds the EC reading stabilized and was read in the digital display meter (Noorikh *et al.,* 2013).

2.8. Determination of Particle Sizes of the Soil Samples

A 50.0 g of the air-dried sample was weighed into a 250.0 mL beaker, followed by addition of 50.0 mL of the prepared calgon into the sample and add 10.0 mL of deionized water. The suspension was stirred vigorously for one minute using a glass rod and allowed to stand for 30 minutes, and was transferred to the sedimentation cylinder and mixed for 15 minutes at a medium speed with a plunger and made up to 1 liter with deionized water. The cylinder was placed in a flat surface and set the time immediately the hydrometer was placed into the suspension. The first reading on the hydrometer (H_1) was taken at 40 seconds after it has settled down. The hydrometer was removed and the first temperature (T_1) was recorded in (^{0}F). The suspension was allowed to stand for 3 hours and the second hydrometer (H_2) and temperature (T_2) in (^{0}F) readings were taken (Bougucos, 1951).

2.9 Determination of Exchangeable Acidity

A 3.0 g of the prepared sample was weighed into a folded filter paper, placed on a conical flask and 50.0 mL of 1.0 N potassium chloride (1.0 N KCl) was poured gently into the solution through the soil in the filter paper and the leachate collected followed by the addition of 5 drops of phenolphthalein indicator in the leachate and titrated with 0.05N sodium hydroxide (NaOH) to pink endpoint, then the volume (mL) of NaOH used was recorded (Noorikh *et al.*, 2013).

2.10 Sample Preparation for the Determination of the Metals (As, Cr, Ni)

2.10.1 Aqua regia (3:1 HCl /HNO_3) digestion method

A 30.0 mL of HCl and 10.0 mL HNO_3 (3:1 v/v) was added to 1.0 g each of the dried sieved (2 mm) soil sample and left to stand for 24 h. The mixture was then heated on a hot plate at 140 ^{0}C to near dryness. The residue was filtered through Whatman No. 41. The solution was then transferred into 50 cm^3 volumetric flask and made to mark with distilled water, then preserved for metal analysis (Tukura *et al.*, 2013).

2.10.2 Nitric acid digestion method

A 1.0 g of each sample was placed in a 250.0 mL conical flask and 10 .0 mL HNO_3 was added, and then heated for about 45 minutes. A 10.0 mL of HNO_3 was then added and heated at a constant temperature of about 120^{0}C until a clear solution was obtained and the volume

was reduced by evaporation to about 5mL. The flask was cooled at room temperature and the mixture was filtered through a Whatman No. 41.filter paper and transferred quantitatively to a 50.0 mL volumetric flask by adding de-ionized (Fabunmi *et al.*, 2014).

2.10.3 Analysis of Soil Samples

Appropriate working standards were prepared for each of the metal solution by serial dilution of the stock solutions. Each of the sets of serial dilutions was then aspirated one after the other into the AAS and their absorbance recorded. The sample solutions were also aspirated one after the other and the absorbance recorded. Calibration curves were plotted for each of the trace metals standard using absorbance against concentrations (ppm) and the actual concentration of the metal interpolated from the curves (Umar, 2013).

3.0 RESULTS AND DISCUSSION

3.1 Soil pH, Electrical Conductivity, particle size, Exchangeable acidity, Organic Carbon and Matter Contents.

Table 3.1: Physicochemical parameters of soil samples

Sample code	Sample A	Sample B	Sample C
pH-H_2O	6.35	5.81	5.60
pH-$CaCl_2$	5.23	5.35	4.78
E.C(µS/cm)	100	240	210
E.A (Meq/100g)	0.83	1.0	0.50
% O.C	1.40	1.49	1.45
% O.M	2.40	2.57	2.50
% clay	11.4	11.4	10.4
% Silt	6.6	5.6	4.6
% Sand	82	83	85
texture class	SL	SL	LS

Table 3.1 showed the results of the physicochemical parameters of the soils. The pH values ranged from 5.60-6.35 at the varying distances in the farmland from moderately to weakly acidic. This might be as a result of the chemicals that are flushed into the water body from the treatment plant and other activities carried out around the farmland that may contribute to the soils acidity. Soil pH regulates almost all biological and chemical reactions in soil (Kabata-Pendias, 2001; Brady and Weil, 2002). Thus the distribution of soil pH may provide a useful index for the potential soil holding capacity for heavy metals, nutrients and fertility of soil

types. The pH of most mineral soils ranges from 5.5-7.5 (Radujevic and Bechkin, 1990; Rashad and Shalby, 2007). Radujevic and Bechkin (1990) explained that acidic soils with pH 4.0-5.5 can have high concentrations of soluble aluminium and manganese ions which may be harmful to the growth of plants Winterhalder (1984) stated that toxicity may occur if soil pH is below 5 and also reported that a pH of approximately 6-7 can release most readily available plant nutrients. The exchangeable acidity value is in the range of 0.5-1.0. The samples organic carbon and organic matter content ranges from 1.40-1.49 and 2.40 to 2.57 respectively. This value is lower than the critical levels required by soils for agricultural use as suggested by Odu *et al*., (1985). Soil accumulation and availability of heavy metals are affected by soil OM, soil pH, grown crop species and crop rotation (IPNI, 2008). The soil particle size analysis showed the soil to be sandyloam-loamy sand. Clay ranged between 10.4-11.4 %, sand between 82.0-85.0 % and silt between 4.6-7.6 %.and electrical conductivity values ranged from 100-240 µS/cm.

3.2 Heavy metal Concentrations

Table 3.2: Heavy Metal Concentrations of the samples (mg /kg) using (Aqua regia (HCl: HNO_3)

Sample code	Cr (mg/kg)	Ni (mg/kg)	As (mg/kg)
A_1	0.338±0.0002	0.143±0.0005	1.111±0.0007
B_1	0.444±0.0013	0.061±0.0006	0.836±0.0017
C_1	0.316±0.0002	0.157±0.0007	1.105±0.0004

A_1-C_1=aqua regia extraction, from 0-15 m to 30-45 m.

Table 3.3: Heavy Metal Concentrations of the samples (mg /kg) using Nitric Acid(HNO_3) methods

Sample code	Cr (mg/kg)	Ni (mg/kg)	As (mg/kg)
A_2	0.375±0.0015	0.166±0.0004	0.252±0.0017
B_2	0.260±0.0016	0.264±0,0014	0.206±0.0006
C_2	0.263±0.0009	0.091±0.0004	0.485±0.0003

A_2-$C_{2=}$Nitric acid Digestion from 0-15 m to 30-45 m

The results of heavy metal concentrations in the irrigated farmland soils listed in Table 3.2 showed the presence of all the three heavy metals, the range of the concentration (mg/kg) of As, Cr and Ni were 0.836-1.111, 0.316-0.444 and 0.061-0.157, respectively, for Aqua regia extraction at varying distances from 0-15 to 30-45 m.

For Nitric acid extraction in Table 3.3, the results ranged as follows: 0.206-0.485, 0.260-0.375and 0.090-0.264, for As, Cr and Ni respectively.

The order of concentration of the metals are: As>Cr>Ni for the aqua regia method while for Nitric acid is: Cr>As>Ni.

This result shows that Aqua regia digestion method (A_1, B_1, and C_1) extracted better compared to nitric acid digestion method (A_2, B_2, and C_2). It was reported by McGrath and Cunliffe (1985) that using aqua regia and block digesters, digestion is faster, more economical and can be very simply modified to suit different types of soil. aqua regia (ratio 3:1 or 4:1 v/v) has been said to extract effectively trace metals in sediments (Tukura *et al.*, 2013). This was also in line with work done by Fabunmi *et al*. (2014). United States of America has the following standard for heavy metal concentrations established for agricultural soils: 0.1, 11 and 72 mg/kg for As, Cr, and Ni, respectively (US EPA, 2014). Tanzania has the following standard for heavy metal concentrations: 1, 100 and 100 mg/kg for As, Cd, Cr, Cu, Hg, Ni, Pb and Zn respectively (TMS, 2007).

All the results obtained from the analysis of the metals showed the level concentration of all the heavy metals analyzed in the soil samples at the various distance to be below the maximum tolerable limits in irrigation farmland recommended by TMS (2007) and US EPA (2014) standard guidelines.

4.0 CONCLUSION

The results of this present study indicated the presence of all the five metals analyzed in the samples at the various distances (0-15, 15-30 and 30-45 m) of the irrigation farmland. The concentration of heavy metals followed the order: As>Cr>Ni for aqua regia method and Cr>As>Ni for nitric acid method. The overall results showed that aqua regia method is a better extracting method for the metals under present study than nitric acid, except for nickel

which showed higher extraction with nitric acid than aqua regia method. The results were all below the maximum tolerable limits for heavy metals in irrigation soils recommended by TMS (2007) and US EPA (2014) standard guidelines, but if the anthropogenic activities continue in river Amba used for irrigation of farmland the heavy metals may exceed the tolerable limits.

REFERENCES

1. Barcelo J, Poschenrieder C. chromium in plants. In: Carati S, Tottarelli F, Seqmi P (eds), *chromium environmental issue*. Francotangati press, Milan; 1997. pp 101-129.
2. Bassi M, Corradi MG., and Realini M. Effects of Chromium (VI) om two freshwater plants, *Lemna Minor* and *pistia stratiotes*. *Morphorlogical observations*, 1990; 62:27-38.
3. Bertin G, Averbeck D. Cadmium: cellular effects, modifications of biomolecules, modulation of DNA repair and genotoxic consequences (a review), *Biochimie*, 2006; 88: 1549-1559.
4. Bodek I, Lyman WJ, Reehl WF, Rosenblat DH. in *Environmental Inorganic Chemistry: Properties, Processes and Estimation Methods*. Pergamon Press, Elmsford, NY, USA, 1988; pp 110 -115.
5. Bougucos G.H. *Soil Agrom. J.*, 1951; 43: 434-438.
6. Brady N, Weil R. The nature and properties of soils, 13th Edition. Prentice Hall. *Upper Saddle River, New Jersey*, USA, 2002; pp 221 228.
7. Cai Y, Zhuang Z. DNA damage in human peripheral blood lymphocyte caused by nickel and cadmium, *Chinese J. Prevent. Medic*, 1999; 33: 75-77.
8. Chandra S, Chohan LKS, Murthy RC, Sexana PN, Pande PN, Gupta SK. Comparative biomonitoring of leachates from hazardous solid waste of two industries using *Allium* test, *Sci. Total Environ.*, 2005; 347: 46-52.
9. Dixit V, Pandey V, Shyam R. Chromium ions inactivate electron transport and enhance superoxide generation in vivo in pea (*Pisumsativon*L cv:Azad) root mitochondria. *Plant Cell Env*., 2002; 25:687-693.
10. DPR-EGASPIN Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN), Department of Petroleum Resources, Lagos, Nigeria. *Environmental Monitoring and Analysis*, 2002; 2(2): 106 – 111.
11. Eflving, DC., Wilson, KR., Ebel, JG. Jr., Manzell, KL., Gutenmann, WH., and Lisk, DJ.(1994). Migration of lead and arsenic in old orchard soils in the Georgan Bay region of Ontario. *Chemosphere*, 29: 2. 407-413.
12. Fabunmi I, Olumodeji O, Uyimadu JP, Adeleye A. Evaluation of the Effectiveness of Different Acid Digestion on Sediments. *International organization of Scientific Research Journal of Applied Chemistry-journal of Applied Chemistry (IOSR-JAC)*, 2014; 7(12): 39-47.
13. Hong AH, Law PL, Selaman, OS. Heavy metal concentration levels in soil at Lake Geriyo irrigation site, Yola, Adamawa State, North Eastern Nigeria. *International Journal of Environmental Monitoring and Analysis*, 2014; 2(2): 106 – 111.
14. IPNI. Crop fertilization and heavy metal accumulation in soils. *Enviro-brief, of the Scientific Staff of the International Plant Nutrition Institute* (IPNI), No 7.Archived from www.ipni.net/publication/envb.nsf/FILE/09062-07-Enviro-Brief-07.pdf on 24 Sept, 2012.
15. Kaasalainen M, Yli-Halla M. Use of sequential extraction to assess metal partitioning in soils, *Environ. Poll.*, 2003; 126, 225–233.
16. Kabata-Pendias A, Pendias H. Trace Metals in Soils and Plants, CRC Press, Boca Raton, Fla, USA, 2nd edition, Australia. *Journal of Environmental Pollution*, 2001; 3:317-323.
17. Khodadoust AP, Reddy KR, Maturi K. Removal of nickel and phenanthrene from kaolin soil using different extractants. *Environmental Engineering Science*, 2004; 21(6): 691–704.
18. Kotas J, Stasicka Z. Commentary: chromium occurrence in the environment, and methods of its speciation. *Environ Pollut*, 2000; 107: 263–283.

19. Li, PH, Kong, SF, Geng CM, Han B, Lu B, Sun RF, Zhao RJ, Bai ZP. Assessing the hazardous risks of vehicle inspection workers' exposure to particulate heavy metals in their workplaces. *Aerosol Air Qual. Res*. 2013; 13: 255–265.
20. Luca DP, Nicola V. Metals Extraction from Contaminated Soils: Model Validation and Parameters Estimation. *CHEMICAL ENGINEERING TRANSACTIONS.* Guest Editor(: Carlo Merli Copyright © 2012, AIDIC Servizi S.r.l., ISBN 978-88-95608-19-8; ISSN 1974-9791, VOL. 28.
21. McGrath, SP, Cunliffe CHA Simplified Method for the Extraction of the Metals Fe, Zn, Cu, Ni, Cd, Pb, Cr, Co and Mn, Soils and Sewage Sludges. *J. Sci. Food Agric*., 1985; 36, 794-798.
22. Meller J. Modern inorganic chemistry. *New York*: Longmans, Green, and Company, print, (1912).
23. Mwegoha WJS, Kihampa C. Heavy metal contamination in agricultural soils and water in Dar es Salaam city, Tanzania. *African Journal of Environmental Science and Technology*, 2010; 4(11): 763-769.
24. National Extraction Industries Transparency Initiatives. Report on Revenue, Deductions and Analysis of Disbursement and utilization of funds of selected State Governments 2007-2011, Nassarawa State, SIAO partners, 2013; pp. 3-5.
25. Noorikh F, Taghreed H, Al-Noor, Nadia HA. Analysis and Assessment of Essential Toxic Heavy Metals, PH and EC in Ishaqi River and Adjacent Soil. *Advances in Physics Theories and Applications*, 2013; Vol.16: 2225-0638.
26. Nriagu JO, Azcue JM. Food contamination with arsenic in the environment. *Adv. Environ. Sci. Technol*., 1990; 23: 121-143.
27. Nunes AM, Zavitsanos K, Del-Conte R, Malandrinos G, Hadjiliadis, N. The possible role of 94-125 peptide fragment of histone H2B in nickel-induced carcinogenesis. *Inorg. Chem*, 2010; 49:5658-5668.
28. Odu CTI, Esuruoso ONO. Impact of degradation Processes on Physical and Chemical Properties of Soils in Delta State of the Niger Delta. *J. Geol. Mining Res*., 1985; In; Oghenero, O. A. (2012); 4(2): 13-22.
29. Olatunde S. Olatunji, Beatrice O Opeolu, Olalekan S. Fatoki and Bhekumusa J. Ximba (2013). Heavy metals concentration levels in selected arable agricultural soils in South Western Nigeria. *International Journal of Physical Sciences*. Vol. 8(11), pp. 421-427, DOI: 10.5897/IJPS12.680.
30. Panda SK, Parta HK. Physiology of chromium toxicity in plants- A Review. *Plant physiol. Biochem*., 1997; 24(1): 10-17.
31. Panda SK, Choudhury I, Khan, MH. Heavy metal induce in lipid peroxidation and affects antioxidants in wheat leaves. *Biol, Plant*. 2003; 46: 289-294.
32. Panda SK. Heavy metal phytotoxicity induces oxidative stress in *Taxitheliums*p. *Curr. Sci*., 2003; 84:631-633.
33. Peryea FJ, Kammereck R. Phosphate enriched movement of arsenic out of leadarsenate contaminated topsoil and through uncontaminated subsoil. *Water Air and soil pollution*, 1997; 93: 243-254.
34. Ponil KB, Sajib C, Dharmendra KS, Polash MS. Distribution pattern of some heavy metals in soil of Silghat region of Assani (India), influenced by Jute Mill solid waste, 2013; http://dx.doi.org/10.1155/2013/609203.
35. Poschendrieder C, Vazquez MD, Bonet A, Barcelo J. Chromium III iron interaction in iron sufficient and iron deficient bean plants. Ultrastructural aspects. *J. Plant Nutr*., 1991; 14:415-428.
36. Rashad M, Shalaby EA. Dispersal and deposition of heavy metals around two municipal solid Waste (MSW) dump sites, Alexandra, Egypt. American *–European Journal of Agricultural and Environmental Science*, 2007; 2 (3): 204-212.
37. Wuana RA, Okieimen FE. HeavyMetals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation; *International Scholarly Research Network* ISRN Ecology, Volume 2011, Article ID 402647, 20 pages, doi:10.5402/2011/402647.
38. Radujevic M, Bechkin. Soil Sludge and Dust. Practical Environmental Analysis. The Royal Society of Chemistry. Cambridge. UK., 1990; 138-150, 303-313.
39. Scragg A, *Environmental Biotechnology*, Oxford University Press, Oxford, UK, 2nd edition; 2006.
40. Suciu I, Cosma C, Todica M, Bolboaca SD, Jantschi L. Analysis of soil heavy metal pollution and pattern in central Transylvania, *Inter. J. Molecul. Sci.*, 2008; 9, 434-453.
41. Tanzania Standards for Receiving Water, Effluents and soils (TZS789:2003). *Tanzania Bureau of Standards, 2003.*

42. TMS. Tanzania Ministry of State.The environmental management (soil quality standards) regulations, Vice President's Office – Environrment, 2007.
43. Tukura BW, Usman NL, Mohammed, HB. Aqua regia and ethylenediaminetetracetic acid (EDTA) trace metal levels in agricultural soil, *Journal of Environmental Chemistry and Ecotoxicology,* 2013; 5(11): 284-291.
44. Umaru PE. Concentration of Heavy Metals in Soil from an Irrigated Farmland in Kaduna Metropolis, Nigeria. *International Journal of Advancements in Research & Technology*, 2013; 2(1): 2278-7763.
45. US EPA. United States Environmental Protection Agency. Cleaning up the Nation's Hazardous Wastes Sites. Office of Solid Waste and Emergency Response, Washington, D.C., 2014.
46. Walkley A, Black IA. An examination of the Degtjareff method for determining organic carbon in soils: Effect of variations in digestion conditions and of inorganic soil constituents. *Soil Science*, 1934; 63: 251-263.
47. Young JA. Zn and Cd in Soil following Irrigation with Untreated Urban Effluents in Arsenic (III) Chloride. *J. Chem. Educ.,* 2006; 83(2): 207.